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PROCEEDINGS OF THE COAL CONVERSION CONTRACTORS' REVIEW MEETING

NOVEMBER 14-16, 1984, CALGARY, CANADA

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[illegible] 1984, CALGARY, CANADA

[illegible] KELLY

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PROCEEDINGS OF THE COAL CONVERSION CONTRACTORS' REVIEW MEETING

NOVEMBER 14-16, 1984, CALGARY, CANADA

EDITOR/ÉDITEUR

JAMES F. KELLY

COMPTE RENDU DE LA RENCONTRE D'ÉTUDE DES ENTREPRENEURS EN CONVERSION DU CHARBON

14-16 NOVEMBRE 1984, CALGARY, CANADA

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FOREWORD

These proceedings describe in detail the status and range of R&D activities in coal conversion supported by Energy, Mines and Resources Canada through CANMET's contract research programs. Government participation is either through the Shared-Cost Energy Conversion Program or the Unsolicited Proposal route. Both programs are administered by the Science Branch of Supply and Services Canada and are highlighted in the February 1985 issue of its Research and Development Bulletin.

The five sessions of these proceedings cover a wide spectrum of CANMET R&D interests from direct coal liquefaction to gasification and coprocessing. However, not all contract work could be included for presentation due to time and budget constraints. Also, the special session on coprocessing (Session V) was not based on contracts but on invited presentations by current leaders in the field.

Some of the major accomplishments of the contract programs since the last contractors' review meeting held in 1982 are discussed. The Sandwell Group have brought their CENTRAX deashing process much closer to demonstration. B.C. Research and NSRFC have been able to continue their programs to evaluate the liquefaction behaviour of their coals. The cooperative program with Japan has evolved into a second stage with a new group of Canadian coal samples sent to Japan for experimental evaluation and study. The production of gasoline from coal rejects has been shown to have economic potential in Western Canada using the gasification-synthesis route. Past emphasis at CANMET on coprocessing has been justified based on the rapidly expanding increase in R&D activity worldwide.

Future directions of the contract program will place increased emphasis on fundamentals both in liquefaction and coprocessing. For coal liquefaction, the aim will be to investigate novel concepts that might lead to reduced capital and operating costs. In coprocessing, there is a need to bridge fundamental gaps with respect to basic understanding of the complex interactions between the simultaneous liquefaction of coal and upgrading of heavy oil.

No attempt was made to enforce a uniform style on the authors. It was felt that due to the wide background among participants from different countries, a more interesting and readable set of proceedings would be obtained with minimum editing. Each session was followed by a discussion period which was recorded and transcripts are included with the proceedings. An updated Contractors' Final Report List and Attendee List are also included for those seeking more information.

James F. Kelly
Head, Coal Liquefaction
Energy Research Laboratories

AVANT-PROPOS

Le compte rendu donne une description détaillée de l'état actuel et de l'envergure des contrats de recherche et développement sur la conversion du charbon appuyés par Énergie, Mines et Ressources par l'intermédiaire des programmes de recherche subventionnés du CANMET. La participation du gouvernement fédéral se situe soit à l'intérieur d'un programme de conversion de l'énergie à frais partagés ou par voie de propositions non sollicitées. Les deux programmes sont gérés par la Direction générale des sciences de Approvisionnement et Services Canada et mis en relief dans le bulletin Recherche et Développement de février 1985 publié par ce Ministère.

Le compte rendu est divisé en cinq parties (5 sessions) qui englobent les principales activités de R-D du CANMET, y compris les procédés de liquéfaction directe du charbon, la gazéification et le cotraitement. Cependant, en raison des délais limités et des restrictions budgétaires, il a été impossible d'inclure des exposés sur tous les travaux effectués à contrat. En outre, l'information contenue dans la partie traitant du cotraitement (Session V) ne provenait pas de rapports d'activités effectuées à contrat mais de présentations données par des spécialistes dans la matière.

Certains des principaux travaux exécutés dans le cadre du programme de recherche à contrat depuis la dernière Réunion d'étude des entrepreneurs tenue en 1982 font l'objet de discussions. Le Sandwell Group a perfectionné son procédé d'élimination des cendres (CENTRAX) au point d'en faire la démonstration prochaine. Le Groupe de recherche de la C.-B. et la N.S.R.F.C. ont pu poursuivre des programmes ayant pour objectif l'analyse du comportement du charbon durant la liquéfaction. L'envoi d'un nouveau lot d'échantillons de charbon canadien au Japon à des fins d'essais et d'évaluation a permis au programme de recherche conjoint avec le Japon de franchir une nouvelle étape. La production d'essence à partir de résidus de charbon semble être économiquement rentable dans l'Ouest canadien au moyen des procédés gazéification-synthèse. L'importance accordée dans le passé au cotraitement par le CANMET se justifie par l'accroissement rapide à l'échelle mondiale des activités de R-D dans ce domaine.

À l'avenir, les objectifs visés par le programme d'activités à contrat comprendront les éléments de base de la liquéfaction et du cotraitement. En ce qui concerne la liquéfaction du charbon, on recherchera des concepts nouveaux qui permettraient de réduire les coûts des immobilisations et les coûts opérationnels. Quant au cotraitement, il est nécessaire d'améliorer la compréhension des interactions complexes entre la liquéfaction simultanée du charbon et la valorisation de l'huile lourde.

Le compte rendu n'a fait l'objet d'aucune révision visant à améliorer le style des auteurs. Vue la vaste expérience des participants des différents pays, on a cru qu'il serait ainsi possible de présenter des exposés plus intéressants. Chaque session a été suivie d'une période de discussions lesquelles ont été enregistrées et dont copie est jointe au compte rendu. Les documents renferment également une mise à jour de la liste des contrats, laquelle fait partie du Rapport final des entrepreneurs, de même qu'une feuille de présence, le tout à des fins d'information.

James F. Kelly
Chef, Section de la liquéfaction du charbon
Laboratoires de recherche sur l'énergie

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SESSION I

DIRECT HYDROLIQUEFACTION

Chairman: M.M. Papic

SESSION I: PAPER 1

THE SANDWELL CENTRAX DEASHING PROCESS

P.G. Groeneweg, S.L. Hodd and G. Teodosiu*
Sandwell Beak Research Group (SBRG)

ABSTRACT

The separation of ash and unconverted coal from products of coal liquefaction or coprocessing of coal and heavy oil/bitumen is a critical operation, significantly affecting the net yield of liquid products. The need for effective and cost-efficient product recovery has stimulated the search for advanced deashing processes. This need is particularly acute for the higher ash lignite and subbituminous coals of western Canada. The Sandwell Centrax Process, by extraction of liquid products from solids using a process-derived extractant in specially configured stages, achieves complete liquid product recovery and liquid free solids.

This paper reviews the importance of effective deashing in liquefaction and coprocessing, the current state-of-the-art in the field, Centrax process concepts and the performance of Centrax deashing on coal liquefaction products derived from Saskatchewan lignite and Illinois #6 bituminous coal. Preliminary economic models are presented that show the Centrax process can reduce the cost of coal liquids by about 20%. Current programs to demonstrate and scale-up the process are also described.

**denotes speaker*

PRÉSENTATION 1

LE PROCÉDÉ D'ÉLIMINATION DES CENDRES SANDWELL CENTRAX

P.G. Groeneweg, S.L. Hodd et G. Theodosiu*
Groupe de recherche Sandwell Beak (GRSB)

RÉSUMÉ

La séparation de la cendre et du charbon non converti des produits provenant de la liquéfaction du charbon ou du cotraitement du charbon et du pétrole lourd/bitume est une opération critique qui affecte sérieusement la production nette de produits liquides. La nécessité d'une méthode de récupération de produits efficace et rentable a stimulé la recherche sur les procédés avancés d'évacuation des cendres. Ce besoin s'avère particulièrement pressant dans le cas du lignite et des charbons sub-bitumineux de l'Ouest du Canada qui produisent plus de cendres. Le procédé Sandwell Centrax, qui consiste à extraire les produits liquides des solides en utilisant un produit d'extraction retiré à des stades spécifiques du processus, permet la récupération complète du produit liquide et des solides libres de liquide.

La communication porte sur l'importance d'un procédé efficace d'élimination des cendres dans la liquéfaction et le cotraitement, l'état actuel des connaissances dans ce domaine, les concepts propres au procédé Centrax et le rendement de ce procédé dans le cas des produits provenant de la liquéfaction du lignite de la Saskatchewan et du charbon bitumineux Illinois nº 6. Les modèles économiques préliminaires qui sont présentés démontrent que le procédé Centrax peut réduire d'environ 20 % le coût des liquides de charbon. On présente également les programmes en cours qui ont pour but de faire la démonstration du procédé et de le réaliser sur une grande échelle.

**indique le conférencier*

THE SANDWELL CENTRAX DEASHING PROCESS

INTRODUCTION

The efficient separation of coal liquids from ash and residual unreacted coal is a long-standing problem in coal liquefaction and a major obstacle to economic production of coal synfuels (1). Overcoming difficulties in deashing coal liquefaction products has been the objective of many research investigations. At the last "Coal Liquefaction Contractors' Review Meeting" we discussed the direction being taken by Sandwell to develop an advanced deashing process aimed at the complete recovery of liquefied products from residual solids. Our approach, called Centrax* separation, represents an innovative approach to the effective recovery of all synthetic hydrocarbons, including oil, asphaltenes and pre-asphaltenes from solids, yielding an essential dry ash concentrate. In the course of our work we have been able to demonstrate at bench-scale the effectiveness of the process with primary coal liquefaction products derived from bituminous coal as well as lignite coals.

The Centrax process has complete flexibility with respect to its use as an inter-stage deashing step or as a final product separation stage after closely coupled two-stage liquefaction. The performance of the process by its very nature is independent of coal type, solids loading, and degree of product hydrogenation over a very wide range of variables.

This paper reviews the current status of Centrax development and describes the on-going development program.

STATE-OF-THE-ART IN DEASHING TECHNOLOGY

Several approaches to deashing have been taken and are discussed here as a background to the Centrax process. The only commercially proven method is by vacuum distillation which serves to recover only distillable oils leaving an unseparable mixture of solids and non-volatile liquid hydrocarbons. In order to reduce the amount of inseparable non-volatile components remaining in the residual products, a high degree of hydrogenation is required prior to separation by distillation. In order to maintain fluidity in the vacuum bottoms, the solids cannot be concentrated above 50%. The residual vacuum bottoms are subsequently gasified to produce process hydrogen.

Advanced processes such as Critical Solvent Deashing and Anti-Solvent Deashing achieve a very high level of solids separation from liquid products at the expense of precipitating some of the asphaltenes and most of the pre-asphaltenes to increase the settling ability of residual solids. The ash concentrate can be concentrated to only about 50-70% requiring its ultimate gasification to obtain some residual value from this material (2).

The direct filtration of primary liquefied coal slurries has proved to be quite difficult as a result of high specific flow resistance giving low average flow rates per unit area. Cycle times for filtration are in the order of three hours. The addition of filter aids does not appear to be beneficial because of quantities required combined with the further additional liquid retained by the expanded cake (1).

Centrifuges have also been tried with mixed success. Although separating efficiencies are higher than with hydrocyclones, high ash levels in the overflow (centrate) still result. The addition of an anti-solvent improves the centrate clarity at the expense of a greater loss of liquid product in the centrifuge cake. A high-quality centrate cannot be achieved if a large proportion of the pre-asphaltenes are to be recovered (3).

Finally, efforts are being made to minimize the need for deashing by removal of mineral matter prior to liquefaction or by achieving high levels of distillate conversion prior to separation as a final stage. While beneficiation will reduce the level of ash in the liquefaction feed, it will not eliminate the need for the removal of solids from liquid products. A change in the mixture of the slurry solids composition could be detrimental to thermal conversion and solids' removal. Coal pretreatment in coal liquefaction or co-processing will in addition be feedstock dependent. Closely coupled two-stage liquefaction reduces the amount of the non-distillable coal liquids prior to deashing. This should improve the operation of solids' recovery but does not eliminate the need for final deashing. This improvement in product recovery is achieved at the expense of catalytic hydrocracking in the presence of solids, and puts some limitation on the final product slate and on the choice of recycle solvent properties.

The ability to recover coal liquids is dependent upon the extent to which the residual solids (ash and unconverted coal) can be concentrated. Figure 1 illustrates the relationship between primary product recovery in coal liquefaction and the final solids concentration in the ash concentrate for both high ash Canadian lignite (20.4% ash MAF and 95.4% conversion, MAF basis) and Illinois #6 coal (12.4% ash and 93% conversion, MAF basis).

This figure also shows that about 20% or more of the gross liquid product remains unrecovered when either vacuum distillation or the external solvent deashing processes are employed. The Centrax deashing process features complete liquid recovery by producing a cake essentially free of all liquids.

**Centrax is a Sandwell and Company Limited registered name.*

CENTRAX PROCESS DESCRIPTION

Complete product recovery is accomplished in the Centrax process by the displacement of all the liquids, including oils, asphaltenes and pre-asphaltenes, from the solids using a specially selected but process-derived extractant. Extraction and separation occurs in one or more integral stages using centrifugal forces to positively settle and compact the cake. All coal-derived liquids are kept in solution by the extractant so that the process asphaltenes and pre-asphaltenes are not co-precipitated with the solids in any part of the process.

In the final stage, the volatile extractant is recovered from the interstitial spaces of the solids cake, yielding a dry and friable ash concentrate. Figure 2 illustrates one arrangement of the Centrax process that achieves the objectives of complete product recovery.

PROCESS FEATURES

The Centrax deashing process features a number of significant and desired features, namely:

- complete product recovery
- minimal energy rejection in ash concentrate
- no external solvent use
- no evidence of retrogressive reactions occurring during deashing
- complete flexibility of incorporation into any coal liquefaction process arrangement
- high throughput.

Each of these is discussed separately.

Complete Product Recovery

The Centrax deashing process is totally effective in recovering oils, asphaltenes and pre-asphaltenes. This has been demonstrated by a simulation of the Centrax process with products derived from Saskatchewan lignite and Illinois #6 bituminous coal. In the case of lignite product deashing, fresh materials were produced in Sandwell's 0.1 TPD PDU using Estevan lignite and separated using the Centrax Deashing Process. The block diagram for this case is shown in Figure 3 along with the results of the separation. An essentially liquid-free ash concentrate was produced.

Another series of tests were conducted with aged samples of products from Run 243 at the Wilsonville 6TPD pilot plant. Illinois #6 bituminous coal was used in this run (4). In this series of tests a large number of Centrax arrangements were studied at the laboratory bench-scale. These tests were conducted to optimize the Centrax process variables with respect to the type and quantity of extractant, process conditions and configuration. Figure 4 illustrates that the Centrax process can achieve an ash concentrate devoid of liquid products. This complete product recovery is significant in view of the short contact time operation (25-50% of normal SRC dissolver residence time) of the Wilsonville plant during Run 243 as reflected in the high concentration of both asphaltenes and pre-asphaltenes in the deashing feed.

Table 1 summarizes the liquid product recovery for both the case of Estevan lignite and Illinois #6 bituminous coal. Within the limits of analytical accuracy, the liquid recovery was essentially 100% for both cases. The process successfully extracted all the fractions, including the pre-asphaltenes, which are not recovered by other processes, and the process-derived extractant.

In both series of tests, the ash concentrate was produced dry and free of liquids and the centrate contained less than 0.1% ash. In the case of the Wilsonville samples, some organic solids were present in the centrate. These solids are denoted as quasi-solids (cresol soluble and THF insoluble) and are likely the result of sample aging. They are expected to be reconverted to liquids upon subsequent upgrading.

Because the Centrax process recovers all liquids essentially free of solids there are numerous advantages in coal liquefaction and coprocessing, namely: easier recycle solvent balancing, greater selectivity of recycle solvent streams including those fractions with well-known, excellent solvent properties, as well as opportunities to tailor downstream processing to the solids-free recovered products.

Minimal Energy Rejection in the Ash Concentrate

Energy rejection is defined as the fraction of feed coal heating value lost with the ash concentrate. It is an excellent measure of the deashing efficiency. The heating value rejected in the ash concentrate is the sum of that available from unreacted coal and unrecovered liquid products and solvents. The minimal level of energy rejection can be achieved by the complete recovery of liquid products.

Figure 5 illustrates the significance of increasing the level of solids in the ash concentrate in order to reduce the amount of energy rejected in the ash concentrate. Centrax deashing results in the minimum loss of energy in the ash concentrate.

It can be argued that the energy remaining in the ash concentrate is required for hydrogen production and thus does not represent an economic loss.

This is not so for several reasons:

- the majority of the energy is in the form of liquid hydrocarbons, which have already undergone at least partial hydrogenation and heteroatom removal;
- due to recent advances in catalyst development for high molecular weight fractions the extra material recovered by Centrax can be upgraded into valuable products;
- in the Canadian economic context, where the production of hydrogen by natural gas reforming is a viable alternative, the complete recovery of liquid has a significant impact on the economics of coal liquefaction, as will be shown later.

No External Solvent

In an attempt to increase the recovery of asphaltenes and pre-asphaltenes, some processes employ the use of external solvents. The use of these solvents adds to the operating cost of deashing and to the capital investment for handling and recovering these valuable materials.

Centrax deashing uses only modest quantities of process-derived solvent as extractants. They are readily recovered in the process without any measurable loss.

Product Stability

One disadvantage of inter-stage deashing for two-stage coal liquefaction which has been experienced by others is the recondensation of reactive coal liquids into high molecular weight products between stages. This is often evident by an increase of asphaltenes, pre-asphaltenes and even unreacted coal between the stages of coal dissolution and hydrogenation. For this and other reasons, closely coupled process configurations are being investigated by several process developers.

One of the major benefits of Centrax deashing is that its process steps tend to stabilize the products so that no evidence of regression into larger molecular weight fractions is found. In fact, Centrax deashing would appear to offer the same advantage as close-coupling, namely: product stabilization and retention of asphaltene and pre-asphaltene for further upgrading, without the need of carrying solids through the catalytic processing stages.

Process Flexibility

In order to make coal liquefaction a versatile and efficient process, it is necessary for the deashing step to be effective for a wide variety of properties as could be expected from various coals and processing conditions. Table 1 has shown that equally complete deashing can be achieved for such diverse coals as Saskatchewan lignite and Illinois #6 bituminous coal. In both cases, products of the non-catalytic solvent extraction process were successfully deashed.

In an extreme test of the Centrax process, primary products of Wilsonville Run 242 were processed. In this run, the coal slurry bypassed the dissolver and received only a short contact time (SCT) reaction in the preheater(5). In this case, for a Centrax process arrangement similar to Run 243 in Figure 4, the final ash concentrate was concentrated up to 98.8% solids, with only a small amount of liquid product rejected.

Thus Centrax technology offers the potential of making solids separation efficient and independent regardless of the severity of initial processing and creates the prospect for upgrading of deashed products, using conventional hydrocracking technology in a solids-free environment.

High-Intensity Deashing

Centrax separation is designed to occur rapidly with minimal space requirement. Separation is accomplished positively and quickly without the need to reduce the volume of material to be deashed by prior vacuum distillation, an operation which is also thought to contribute to product degradation.

ECONOMIC IMPACT OF IMPROVED DEASHING

The benefits of improved deashing technology are not illusory. A study conducted by Mitre Corporation (2) concluded that in the general range of deasher performance, each per cent reduction in the rejection of liquid 450°C plus material results in about a 1% reduction of the final product cost.

Our own study of the economics of two-stage liquefaction with Centrax deashing confirms this estimate. Figure 6 shows the positive impact of Centrax deashing on the cost of producing liquid fuels from lignite. The before tax cost per barrel of coal liquid product for two levels of solid separation efficiencies and associated coal liquefaction processing configurations have been computed using an interactive coal liquefaction financial model. The model calculates the cost per barrel on a 20-year life and levelized cost basis as applied to the case of two-stage liquefaction with inter-stage deashing. Costs have been divided into capital charges, coal costs, other operation costs and the cost of purchased natural gas, if required.

In case A, the ash concentrate contains 57% solids which are gasified to produce process hydrogen. Case B is defined by 100% product recovery, as can be achieved by Centrax deashing, with hydrogen generated by gasification of coal and residuals. Cases C and D examine the cost advantage of steam reforming natural gas, an option made possible by efficient Centrax deashing. A natural gas price of $4.00 and $2.00 CDN/1000 SCF is used in cases C and D, respectively.

This model confirms that product recovery through more effective deashing results in a substantial reduction in the cost of synthetic coal liquids. Centrax deashing results in a lower cost per barrel of liquid product due to a reduction in plant investment, amount of coal required and other operating costs. Hydrogen generation by natural gas further reduces capital costs and coal requirements.

Figure 7 illustrates even more dramatically the impact of complete deashing by examining the before-tax return using a discounted cash flow model at a debt/equity ratio of 40/60. The internal rate of return for a coal liquefaction project can be increased by 7% due to complete product recovery by Centrax and up to 16% if natural gas at $2.00 CDN/1000 SCF is used in place of gasification.

The economics of coal liquefaction is highly dependent on the effectiveness of the deashing step. Complete liquid product recovery unique to Centrax deashing, impacts beneficially on the economics of coal liquefaction, making it an economically attractive route to producing new liquid fuels.

FURTHER DEVELOPMENT OF CENTRAX TECHNOLOGY

The technical and economic benefits of Centrax deashing are such that it provides a strong incentive to proceed with its development.

The strategic advantages of Centrax deashing, such as the options for hydrogen production from gas, flexibility in location of the deashing step, obviation of the need to beneficiate coals, greater product mix capabilities and simpler and proven plant unit operations, put the Centrax at the center of liquefaction process improvements.

At present a prototype Centrax separation/extraction unit is nearing completion and is planned to be operational later this month. The prototype unit has a throughput capacity compatible on an intermittent basis with Sandwell's 0.1 TPD coal liquefaction PDU and with much larger units on a continuous basis. Our program in 1985 calls for further process and hardware development and demonstration of the Centrax process.

ACKNOWLEDGEMENT

The authors of this paper would like to acknowledge the contribution of a number of co-workers at Sandwell Research to the Centrax development. The cooperation of Norman C. Stewart of the Electric Power Research Institute in providing samples from the Wilsonville pilot plant is very much appreciated. The Centrax development has been co-funded by CANMET.

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TABLE

Table 1 – Centrax liquid product recovery – test results

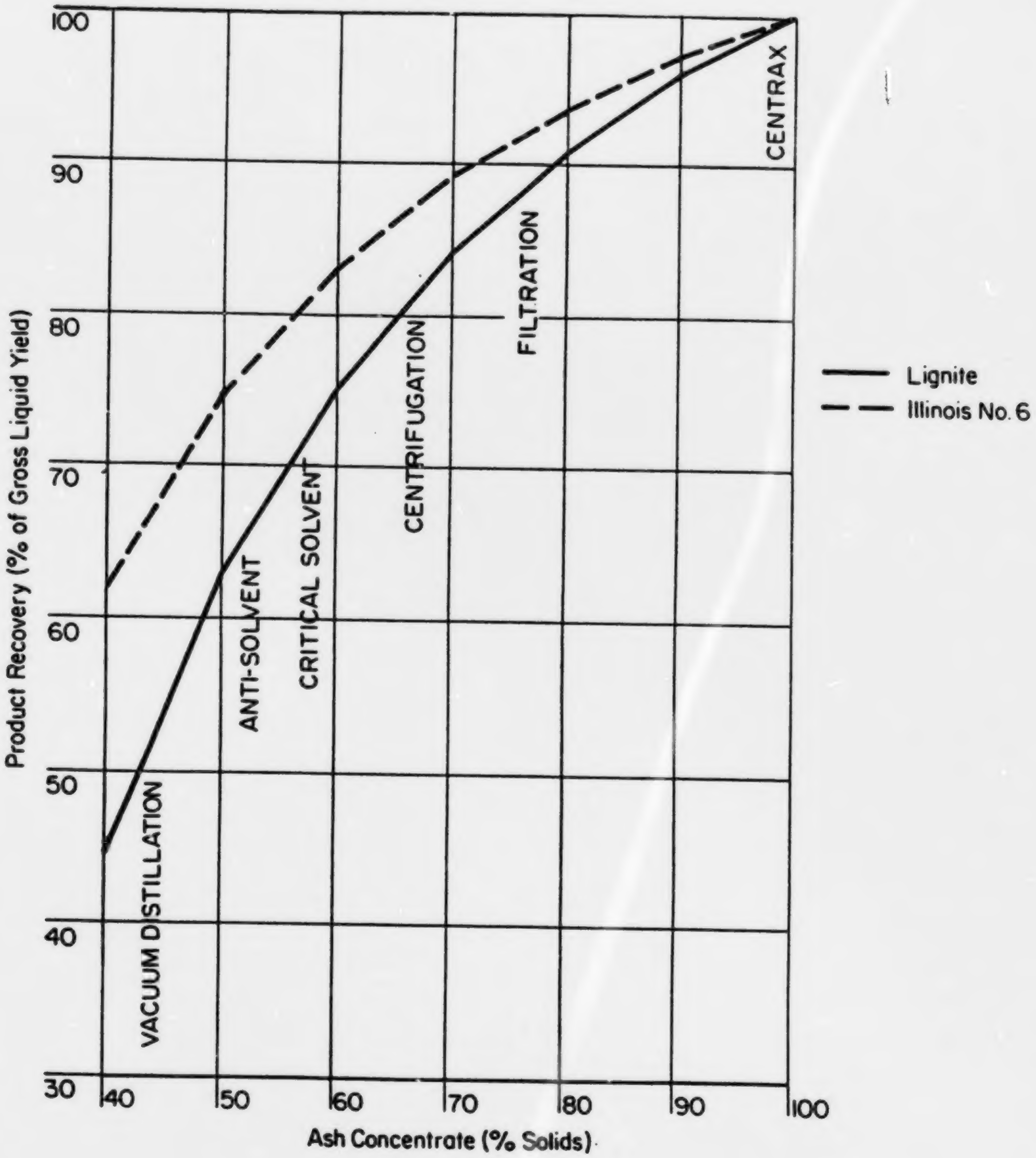
Feed slurry component	Lignite (Estevan)*				Bituminous (Illinois #6)**			
	Feed	Overflow	Ash conc.	Recovery	Feed	Overflow	Ash conc.	Recovery
Oils	88.0	89.1	nil	101.3%	50.2	49.6	nil	98.8%
Asphaltenes	4.3	3.6	nil	83.7%	24.2	23.3	nil	96.3%
Preasphaltenes	2.4	2.0	0.01	83.3%	15.2	14.8	nil	97.4%
Total liquids	94.7	94.7	0.01	100.0%	89.6	87.7		97.9%
						2.9***		to 101.1%***
Solids	5.3	0.1	5.2		10.4	0.1	9.3	
Total	100.0	94.8	5.2		100.0	90.6	9.3	
Extractant	X	X		100.0%	X	X		100.0%
Solids in Ash Concentrate			99.8%				100.0%	

* *Products of Sandwell's 0.1 TPD Continuous Coal Liquefaction PDU*

** *Samples from Run 243 Wilsonville 6 TPD pilot plant*

*** *Quasi-solids (not present in fresh samples, part of liquid fraction)*

FIGURES



	Lignite	Illinois No.6
Ash (% MAF)	20.4	12.4
Conversion (% MAF)	95.4	93.0
Gross Liquid Yield (% MAF)	67.0	76.0

Fig. 1 – Product recovery vs ash concentrate

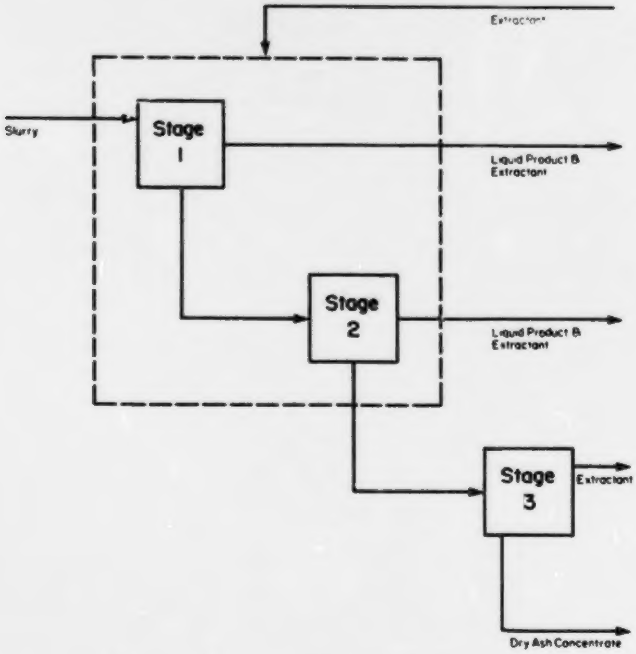
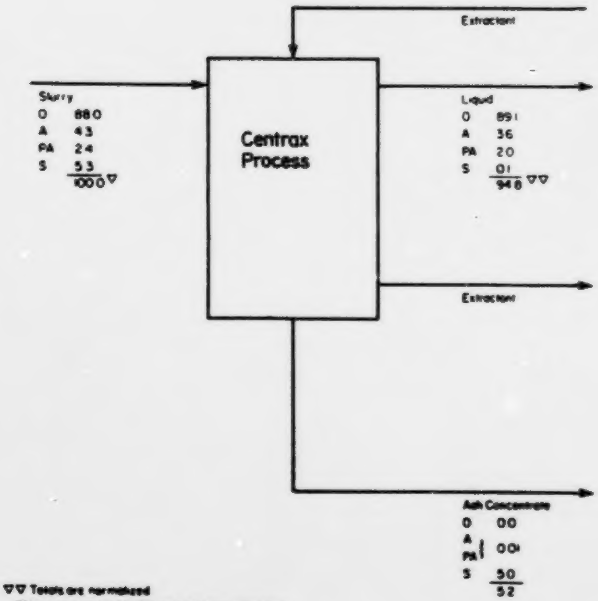

Extractant
Slurry
Stage 1
Liquid Product & Extractant
Stage 2
Liquid Product & Extractant
Stage 3
Extractant
Dry Ash Concentrate

Fig. 2 – Centrax deashing process


Extractant
Slurry
O 88.0
A 4.3
PA 2.4
S 5.3
100.0 ▽
Centrax Process
Liquid
O 89.1
A 3.6
PA 2.0
S 0.1
94.8 ▽▽
Extractant
Ash Concentrate
O 0.0
A PA 0.01
S 5.0
5.2

▽▽ Totals are normalized

▽ Units are scaled to 100 units of slurry feed to the Centrax Process on a weight basis

Fig. 3 – Separation of lignite-derived liquefied coal slurry (SBRG PDU product)

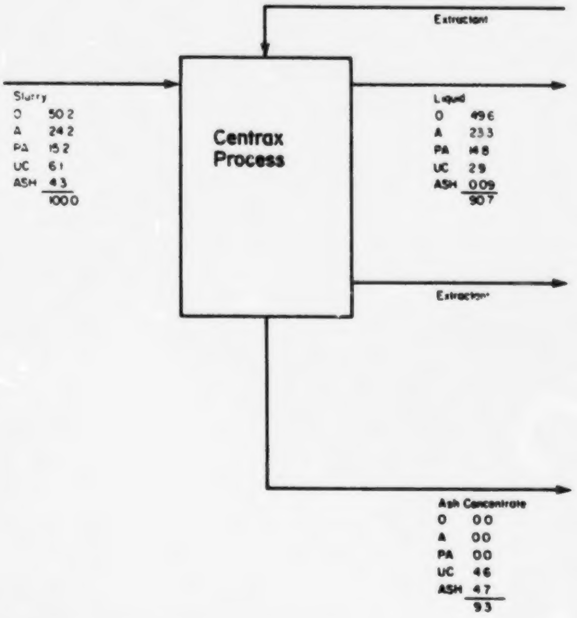
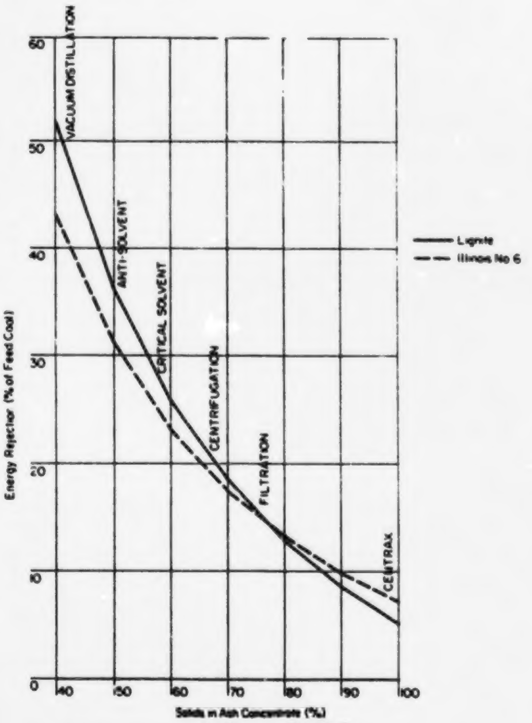
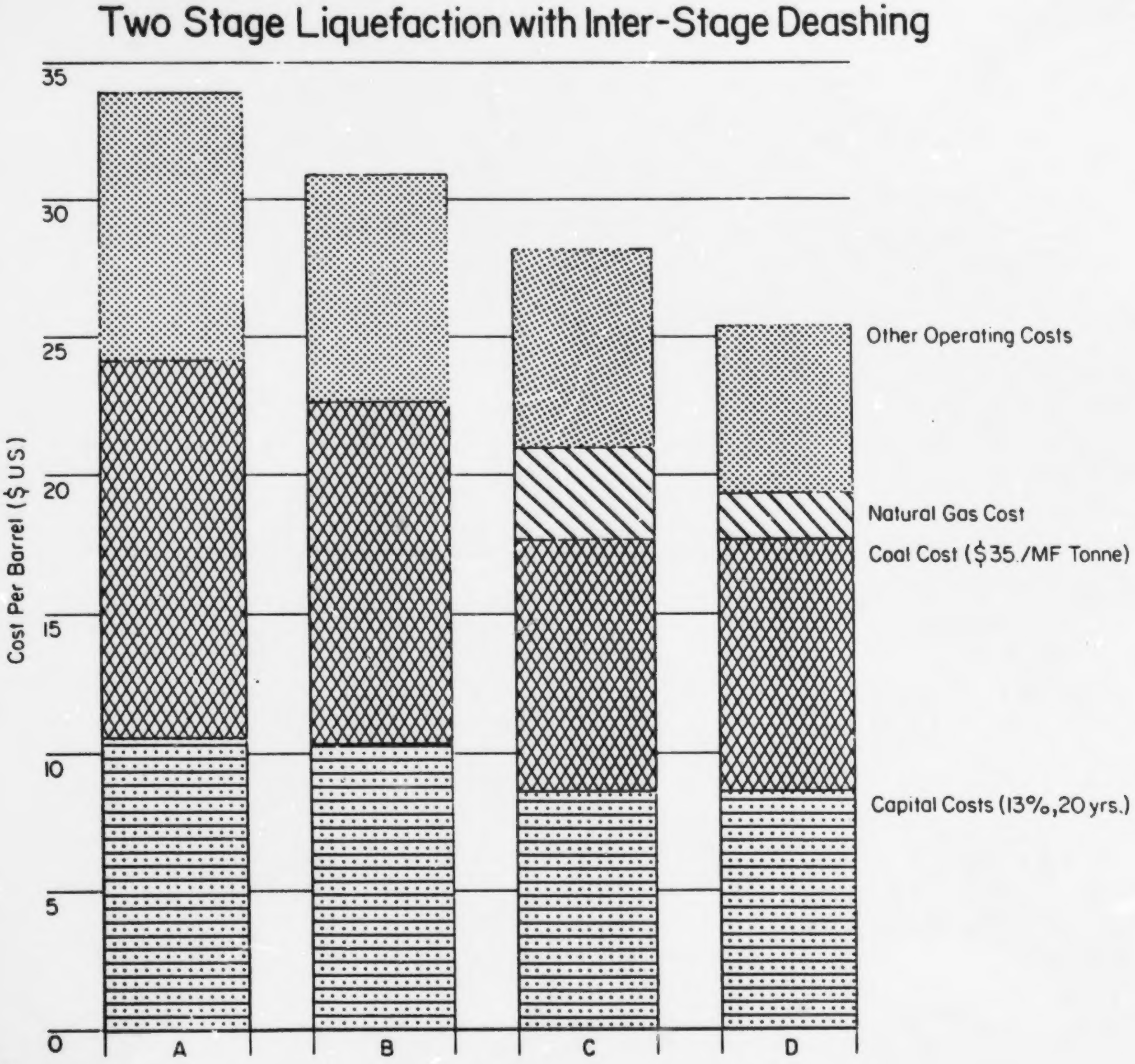

Extractant
Slurry
O 50.2
A 24.2
PA 15.2
UC 6.1
ASH 4.3
100.0
Centrax Process
Liquid
O 49.6
A 23.3
PA 14.8
UC 2.9
ASH 0.09
90.7
Extractant
Ash Concentrate
O 0.0
A 0.0
PA 0.0
UC 4.6
ASH 4.7
9.3

Fig. 4 – Separation of Illinois No. 6 bituminous-derived liquefied coal slurry (Wilsonville samples, run 243)



	Lignite	Illinois No 6
Ash (% MAF)	20.4	12.4
Conversion (% MAF)	95.4	93.0
Gross Liquid Yield (% MAF)	67.0	76.0

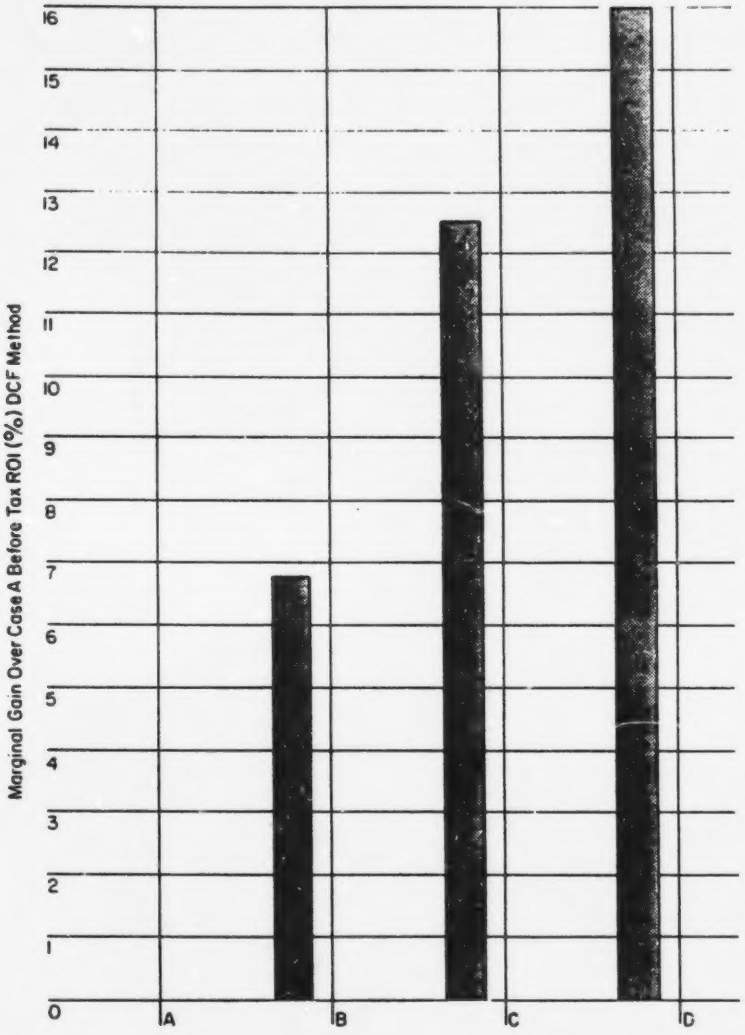
Fig. 5 – Energy rejection vs ash concentrate



CASE DEFINITION				
Ash Concentrate (% Solids)	57%	100%	100%	100%
Residuals	Gasified	Gasified	Fuel	Fuel
H_2 Generation	Residuals	Residuals & Coal	Natural Gas	Natural Gas
Price of Gas ($ CDN/1000 SCF)	—	—	$4.00	$2.00

Fig. 6 – Impact of deashing performance on the cost of lignite synfuels

Debt/Equity Ratio	40/60
Interest	13%
Coal	$35/MF Tonne
Plant Life	20 Years



CASE
DEFINITION

Ash Concentrate (% Solids)	57%	100%	100%	100%
Residuals	Gasified	Gasified	Fuel	Fuel
H_2Generation	Residuals	Residuals & Coal	Natural Gas	Natural Gas
Natural Gas Price ($CDN 1000 SCF)	—	—	$4.00	$2.00

Fig. 7 – Impact of deashing performance on before-tax financial rate of return

SESSION I: PAPER 2

CONTINUOUS BENCH UNIT LIQUEFACTION OF HAT CREEK SUBBITUMINOUS COAL

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ABSTRACT

Hat Creek (B.C.) subbituminous coal was treated in a continuous 1 L/h bench autoclave unit using pre-hydrogenated solvent. Liquid phase products, separated by counter-current centrifugation with THF solvent, were hydrotreated in a 1 L/h fixed-bed continuous hydrotreater. Locked cycle, four-stage tests were done in which startup solvent was a wide cut (+180°C) hydrogenated creosote oil; recycle solvent for succeeding cycles was topped (+180°C) hydrotreated product.

Fourth-stage products from this sequence approached equilibrium with respect to product composition, coal conversion (> 90% daf under optimum conditions) and primary product bottoms which were recycled without hydrotreating.

Results are presented for overall hydrogen consumption, and byproduct gas composition. Analyses of net liquid product (naphtha and middle distillate) are presented and discussed.

**denotes speaker*

PRÉSENTATION 2

INSTALLATION DE LIQUÉFACTION EN CONTINU DU CHARBON SUB-BITUMINEUX DE HAT CREEK, À L'ÉCHELLE DU BANC D'ESSAI

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RÉSUMÉ

On a traité du charbon sub-bitumineux de Hat Creek (C.-B.) dans un autoclave au banc de 1 L/h en continu, utilisant du solvant pré-hydrogéné. Les produits de la phase liquide, séparés par centrifugation à contrecourant avec un solvant THF, ont été hydrotraités dans un hydrotraiteur en continu à lit fixe de 1 L/h. Des essais à quatre étapes, en cycle fermé, ont été faits; le solvant de démarrage était un pétrole de créosote hydrogéné (+ 180°C) très dilué, et le solvant de recyclage pour les cycles successifs était un produit hydrotraité de tête (+ 180°C).

Les produits de la quatrième étape de cette séquence se rapprochaient de l'équilibre relativement à la composition du produit, à la conversion du charbon (> 90 % daf dans des conditions optimales) et aux fonds de produit primaire qui furent recyclés sans hydrotraitement.

Les résultats concernant la consommation générale d'hydrogène et la composition du gaz obtenu comme sous-produit sont présentés. Les analyses des produits liquides nets (naphte et distillat moyen) sont présentées et examinées.

**indique le conférencier*

CONTINUOUS BENCH UNIT LIQUEFACTION OF HAT CREEK SUBBITUMINOUS COAL

INTRODUCTION

Background

British Columbia has large resources of coal in all ranks from subbituminous to anthracitic (see Fig. 1), as well as some poorly defined lignite resources. However, results of a reactivity survey (1) indicated that most of the currently mined coal is not suitable for direct liquefaction.

Currently mined coals from northeast and southeast B.C. are essentially all of low- to medium-volatile bituminous rank and are mainly sold as coking coals. Tests on these coals indicated relatively low total conversions and poor yields of distillate *oils*.

In other areas of the province there are deposits of high-volatile bituminous coals which show much more favourable response to direct liquefaction. None of these coals are, however, currently mined. Deposits which are being developed are those which – for reasons of location and/or low mining cost – are expected to be saleable into Pacific Rim thermal coal markets.

Hat Creek coal showed good reactivity in initial direct liquefaction tests. Due to its low rank, high mineral matter content, and poor response to conventional beneficiation methods, it is not a likely candidate for export as solid fuel. Studies and preliminary planning for a mine-mouth thermal generating plant have been completed, but the provincial electricity supply situation is such that a development of this type is at least a decade away. In any event, reserves at the site are large enough to support both power generation and liquefaction on a large scale.

A feasibility study of indirect liquefaction by SASOL technology with concurrent thermal power generation has been completed and recently published (2). The current work on direct liquefaction is complementary to this published work since – to evaluate alternative development schemes – it is necessary to have suitable test data on the coal to be used.

General information on the Hat Creek depost is presented in Table 1 and its location is shown in Figure 1. It is worthwhile to note that much of the infrastructure required for major development is already in place. Existing roads, rail and pipelines are adjacent or conveniently accessible to the site. Availability of these facilities is an important factor in comparison of alternate energy developments. Coal conversion itself may be a relatively costly technology compared to – for example – distillation of light crude oil. However, if the oil supply requires a massive investment in infrastructure, the overall least cost option may well be to use the accessible resource.

Objective

The objective of the current work on Hat Creek coal is to develop a base of technical information on direct liquefaction of Hat Creek coal so that this option can be considered in comparison to other liquid fuel supply options. Specific aspects include:

- identification (or development) of suitable direct liquefaction technology
- determination of practical operating conditions and raw material utilization
- determination of yields and product slates.

MATERIALS AND METHODS

Representative coal analyses are presented in Table 2; schematics of the bench-scale continuous liquefaction unit and hydrotreater are presented in Figures 2 and 3.

Start-up solvent for reported testwork was hydrotreated creosote oil, after distillation to remove all material boiling below ~180°C.

The locked cycle procedure for separation of net product, residue and recycle solvent is shown in Figure 4.

RESULTS AND DISCUSSION

System Operation

With reference to Figure 4, feed to the hydrotreater was not the total soluble fraction of reactor product. After distillation, removal of the tetrahydrofuran (THF) solvent and cooling to ambient temperature, an insoluble sludge was precipitated. The hydrotreater feed system was not capable of feeding this material as a uniform slurry due to the lack of agitation/recycle, so the sludge – separated by centrifugation – was recycled with hydrotreated, distilled solvent.

It should also be noted that the liquefaction unit (Fig. 2) is single stage and totally back-mixed. Thus short circuiting of feed through the system is an important factor. Longer nominal residence times were required than in batch tests to minimize the amount of material passing through the reactor with inadequate residence time. The importance of this problem with a single-stage reactor will be discussed below in comparison to batch test results.

Locked Cycle Test Results

Table 3 presents the results of a four-stage locked cycle test on Trench B coal which was partially beneficiated in the laboratory (see Table 2).

These results clearly show that high total conversions are obtainable under the indicated test conditions.

The discrepancy in conversion data between gravimetric and calorific values is due to the specious contributions of mineral matter components to *volatile matter* and *fixed carbon* contents of coal as measured by conventional proximate analyses. The largest component of mineral matter in Hat Creek coal is clay which decomposes, releasing its structural water on heating to 900°C. Thus, calorific value (CV) conversion (residue versus feed coal) is a more valid measure of conversion. However, weight data are still required to compute CV conversion and the ash balance conversion can be obtained more rapidly for test evaluation.

Imperfect control over the solvent hydrotreating operation is shown by the variations in tetralin:naphthalene ratio of the recycle solvents used. These data suggest that total conversion is insensitive to solvent donor content above some as yet unidentified minimum value.

Similar results were obtained for Trench A coal.

Product Slate

Atmospheric distillation data for water-free, fourth-cycle hydrotreater product from Trench B coal are presented in Table 4. These results indicate that ~24% of hydrotreater liquid is light material – i.e., boiling below ~200°C – which is not suitable for recycle and must be regarded as part of net product.

Thermogravimetric analyses of the +200°C hydrotreated material indicate that this is also good quality material as indicated by low content of non-distillables (3.4%) and low carbon residue (0.7%).

Table 5 shows the weight distribution of liquefaction products from feed coal. These data show that to maintain the required weight of recycle solvent, only 20-25% of the gross liquid product can be removed as net product. The observed gas plus light liquid yields are equal to or slightly larger than the allowable net offtake. Thus, under the test conditions, the only net products are hydrocarbon gases and light distillate.

Table 6 shows the composition of light distillate from second-stage hydrotreater product as determined by gas chromatography/mass spectroscopy (GC/MS). Roughly two thirds of this material consists of readily identifiable hydrocarbons which would not require further upgrading for use as motor gasoline feedstock. It will also be noted that ibp-180°C material accounted for ~40% of total liquid in this test, which indicates the need for careful control of hydrotreater operation to maintain recycle solvent inventory.

Distribution of net product by calorific value is shown in Table 7. From the data it is clear that C_1-C_4 hydrocarbon gases are a significant co-product. Most of (>90%) of these gases are generated in the liquefaction stage and gas production is roughly porportional to residence time at reaction temperature (440°C). The range of 12-20% is derived from batch (tubing bomb) tests of 25 and 60 minutes duration at which total conversions of >90% are obtained. The high (20%) hydrocarbon gas production value relates 60-minute batch tests and to the continuous unit which – to minimize short circuiting – is operated at a nominal residence time of ~1 h. It is expected that in a continuous reactor designed for (approximately) plug flow, better control of residence time would allow the lower range of hydrocarbon gas production to be obtained.

It is of interest to note that the higher range of hydrocarbon gas production would allow an overall process to generate required hydrogen by steam reforming of co-product gas. Thus, while present relative fuel prices would favour maximum liquid production and purchase of methane for hydrogen manufacture, the overall process could be self-sufficient in gas supply.

Hydrogen Consumption

Due to limitations on accuracy of gas measurement, and experimental emphasis on obtaining high conversions, hydrogen consumption is the least well-defined parameter in the study to date. Overall, hydrogen consumption is estimated to be ~4% versus daf coal (3% versus dry, clean coal) with about one third of the hydrogen consumed in liquefaction and two thirds consumed in hydrotreating. Depending on conditions, hydrocarbon gas yields can be sufficient to provide all the hydrogen necessary, although higher total product value may be obtained by separation and marketing of C_2-C_4 gases.

CONCLUSIONS AND DIRECTION OF CURRENT WORK

The results presented indicate clearly that direct liquefaction is a technically viable process for conversion of (low quality) Hat Creek coal to light distillate and hydrocarbon gas products.

As a potential synthetic fuel development site, the Hat Creek deposit has advantages including large reserves, low mining costs, and existing infrastructure which would compensate to some degree for the cost of two-stage liquefaction.

Current laboratory work on Hat Creek coal is directed towards obtaining detailed material balances, especially in regard to hydrogen consumption, and to optimization of liquid product yield and quality.

REFERENCES

1. Gutierrez, L., Jezko, J. and McElroy, R.O. "Direct liquefaction behaviour of B.C. coals. Coal: phoenix of the '80s", *Proceedings 64th CIC Coal symposium* – A.M. Al Tawell, Editor, C.S.Ch.E., Ottawa, 1982.

2. Hat Creek Coal Liquefaction Project, "Study Committee Report", B.C. Energy Development Agency, June 1981.

3. Kaiser Engineers/Electric Power Research Institute, "Coal Cleaning Tests on Hat Creek Raw Coal for B.C. Hydro", Dec. 1982.

TABLES

Table 1 – Hat Creek coal – general description

Reserves: ~4 × 10^9 tonnes (high ash, subbituminous)

Transport access:
Rail: Minesite
Highway: Minesite
Water: ~16 km (North Thompson River)
Power: Minesite
Pipelines: (gas & oil) ~16 km

Social infrastructure: Existing towns within commuting distance

Climate: Semi-arid, interior plateau

Alternate uses: Power generation
Conversion (direct or indirect liquefaction)

Table 2 – Hat Creek coal proximate analyses

		Dry basis, wt %		
		Volatile matter	Fixed carbon	Ash
Trench A	Run of mine	31.1	25.5	43.4
	Laboratory Beneficiated (Reject, 62% ash)	35.5	33.3	31.3
Trench B	Run of mine	34.7	30.1	35.2
	Laboratory Beneficiated (Reject, 53% ash)	36.4	37.4	26.2
Mine test blend*	9.4 mm × 0.6 mm (⅜ in × 28 mesh)	------------- ND**	--------------	30.6
	WOC product	------------- ND	--------------	20.7
	WOC tailing	------------- ND	--------------	57.7
	0.6 mm × 0.15 mm	------------- ND	--------------	40.6
	WOC product	------------- ND	--------------	26.1
	WOC tailing	------------- ND	--------------	56.7

* *EPRI-CCTF data (3)*
** *not determined*

Table 3 – Trench B coal – locked cycle test data

	Solvent TN*		Total conversion		Weight recovery
	Initial	Final	Ash balance (wt %, daf)	Calorific value (%)	(% of feed)
C-25, 26	2.7	ND	90	92	~94
C-27	2.2	0.9	90	92	93
C-28	5.6	1.3	92	96	93
C-30	3.8	ND	92	95	96

* *Tetralin:Napthalene ratio (index of solvent donor capability)*

Table 4 – Hydrotreater product distillation

IBP – 105°C	0.6% (wt)
105 – 165°C	4.1%
165 – 180°C	6.2%
180 – 200°C	13.1%
IBP – 200°C	24.0%
+200°C	76.0% (TGA non-distillable 3.4%) (TGA carbon residue 0.7%)

Table 5 – Weight distribution of coal liquefaction product

Dry coal (100)	Residue (mineral & organic)	~30%
	CO_2	12%
	C_1-C_4 gas	2-4%
	C_5+ liquid	54-56%

Solvent: Dry coal feed ratio ~2

Allowable net liquid product = 20-25% of gross liquid

IBP-200°C product ≈24% of gross liquid

Table 6 – Light liquid product composition by GC peak area (Hydrotreated second recycle)

	% of total	% IBP–decalin
Toluene	0.95	2.3
Xylenes	4.25	10.2
Trimethyl benzene	1.46	3.5
Phenol	1.09	2.6
Indan	17.6	42.2
Cresols	0.72	1.7
Decalins	0.72	1.7
Identified	26.8	64.2
Unidentified	14.9	35.8
Total	41.7	100.0

Table 7 – Net product distribution by calorific value

	% total CV
Coal (16.27 GJ/tonne as tested)	100
Residue	~6
C_1-C_4 hydrocarbons	12-20
Liquid	74-82

FIGURES

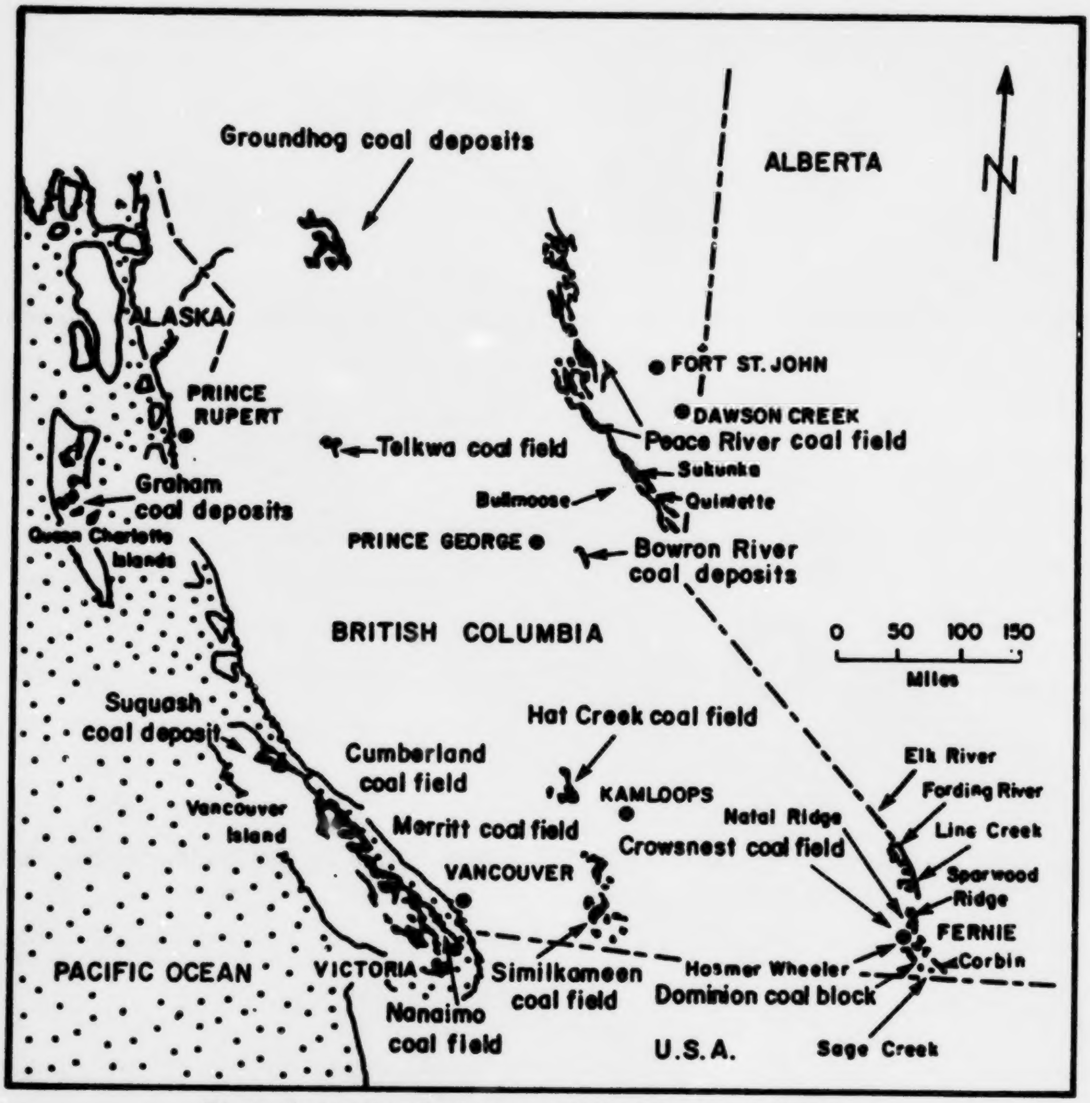

Groundhog coal deposits
ALBERTA
N
ALASKA
PRINCE RUPERT
FORT ST. JOHN
DAWSON CREEK
Telkwa coal field
Peace River coal field
Sukunka
Graham coal deposits
Bullmoose
Quintette
Queen Charlotte Islands
PRINCE GEORGE
Bowron River coal deposits
BRITISH COLUMBIA
0 50 100 150
Miles
Suquash coal deposit
Hat Creek coal field
Cumberland coal field
KAMLOOPS
Elk River
Fording River
Vancouver Island
Natal Ridge
Merritt coal field
Line Creek
Crowsnest coal field
VANCOUVER
Sparwood Ridge
FERNIE
Corbin
PACIFIC OCEAN
VICTORIA
Similkameen coal field
Hosmer Wheeler
Dominion coal block
Nanaimo coal field
U.S.A.
Sage Creek

Fig. 1 – Geographic distribution of British Columbia coal resources

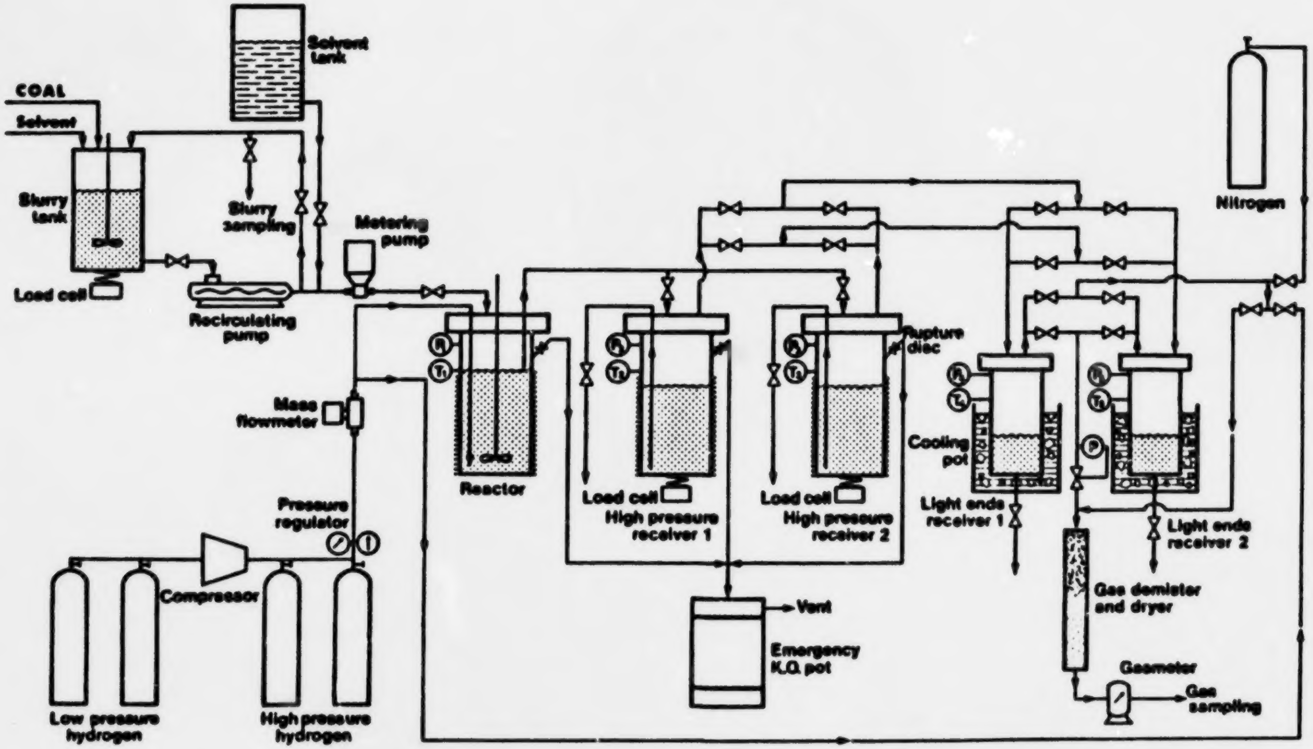

COAL
Solvent
Slurry tank
Load cell
Solvent tank
Slurry sampling
Recirculating pump
Metering pump
Mass flowmeter
Pressure regulator
Compressor
Low pressure hydrogen
High pressure hydrogen
Reactor
Load cell
High pressure receiver 1
Load cell
High pressure receiver 2
Rupture disc
Vent
Emergency K.O. pot
Cooling pot
Light ends receiver 1
Light ends receiver 2
Gas demister and dryer
Gasmeter
Gas sampling
Nitrogen

Fig. 2 – B.C. Research continuous coal liquefaction unit

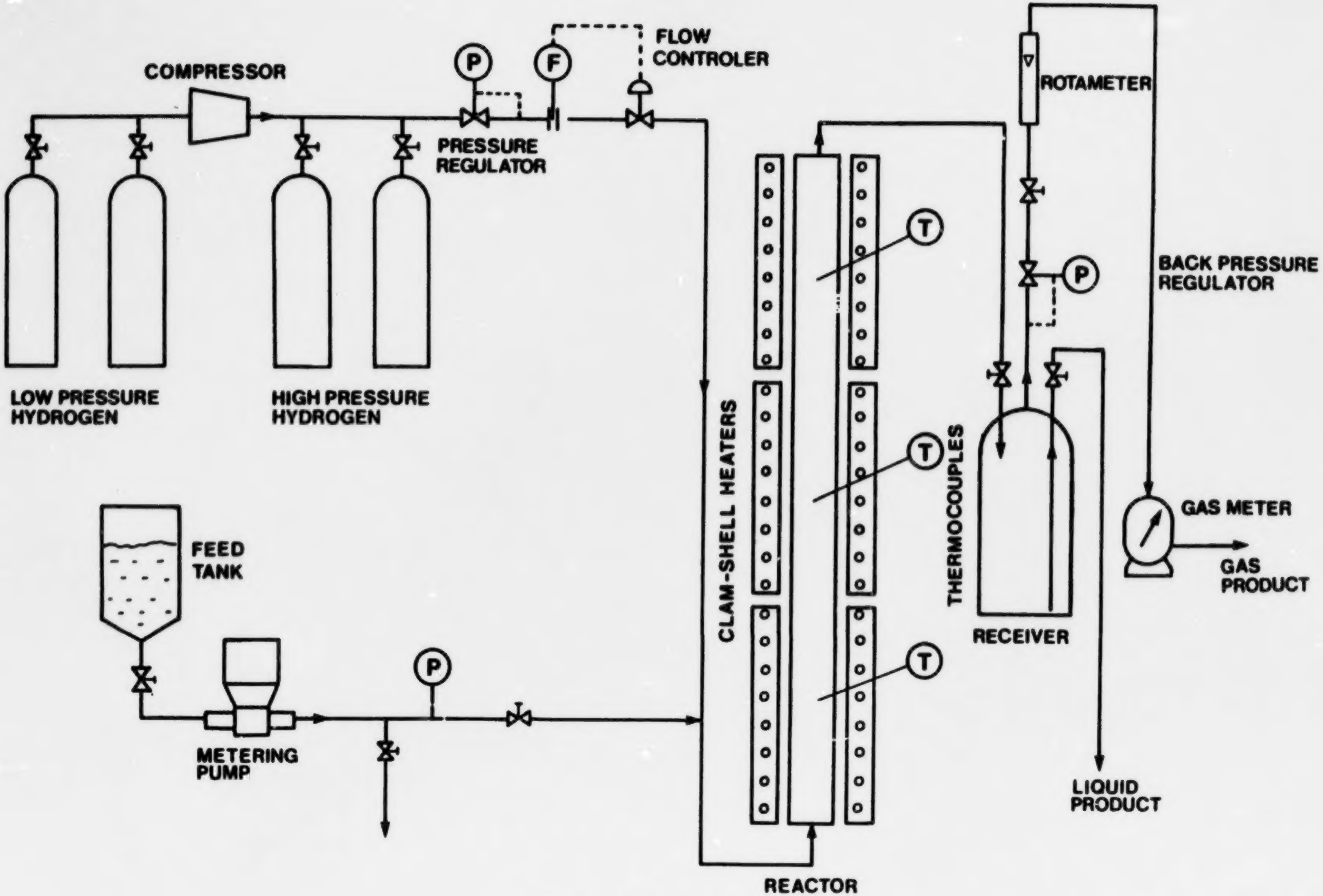
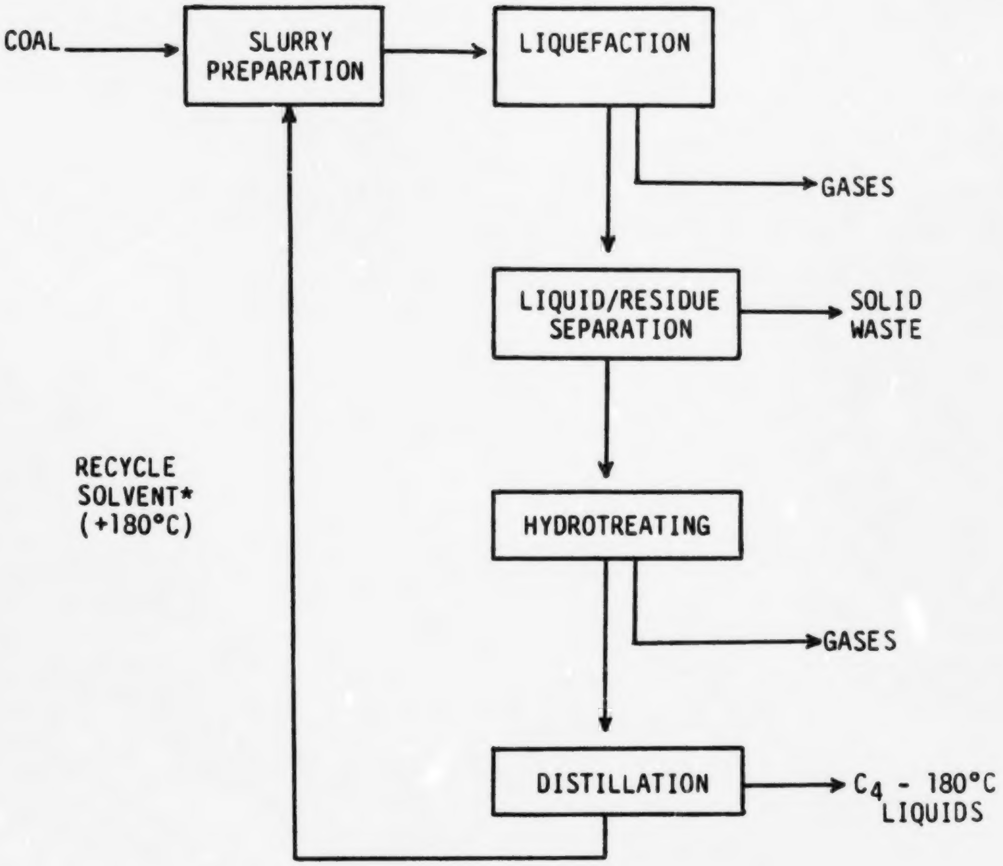

COMPRESSOR
FLOW CONTROLER
P
F
PRESSURE REGULATOR
ROTAMETER
LOW PRESSURE HYDROGEN
HIGH PRESSURE HYDROGEN
T
P
BACK PRESSURE REGULATOR
CLAM-SHELL HEATERS
THERMOCOUPLES
GAS METER
FEED TANK
GAS PRODUCT
RECEIVER
P
METERING PUMP
LIQUID PRODUCT
REACTOR

Fig. 3 – B.C. Research hydrotreater


COAL
SLURRY PREPARATION
LIQUEFACTION
GASES
LIQUID/RESIDUE SEPARATION
SOLID WASTE
RECYCLE SOLVENT* (+180°C)
HYDROTREATING
GASES
DISTILLATION
C4 - 180°C LIQUIDS

*STARTUP SOLVENT = HYDROTREATED CREOSOTE OIL.

Fig. 4 – Locked cycle test sequence

SESSION I: PAPER 3

STUDY RELATING TO THE TECHNICAL AND ECONOMIC FEASIBILITY OF LIGNITE LIQUEFACTION IN SASKATCHEWAN

J.A. Mikhlin, F.A. Ashraf and J.A. Dhawan*
SNC Inc.

ABSTRACT

The study was carried out by SNC Inc., in 1981-82 on behalf of Saskatchewan Oil and Gas Corporation (SASKOIL) and Canada Centre for Mineral and Energy Technology (CANMET). The study included review and evaluation of advanced coal liquefaction processes in all three major routes (direct liquefaction, indirect liquefaction and pyrolysis) for designated Saskatchewan lignites. Assessment of coal gasification processes being developed (or commercialized) in the USA, FRG and UK for production of synthesis gas from the designated lignites (first step of indirect liquefaction) was also included in the study. In addition, preliminary evaluation of the processes and concepts in coal liquefaction considered for commercialization around 1995 was carried out.

Two Saskatchewan lignites, Estevan and Willow Bunch as-received, were designated as a feedstock (Ash 15.4 wt % and 21.0 wt %, dry lignite basis, correspondingly; moisture 35 wt % for both lignites). No pretreatment/beneficiation of the lignites was considered in the study.

Technical assessment, prescreening and ranking in each route for both Estevan and Willow Bunch lignites followed by comparative techno-economic evaluation of selected processes for designated Willow Bunch lignite were carried out for advanced processes. A commercially proven SASOL-type Fischer-Tropsch process (South Africa) was also considered for comparison.

Twenty-five thousand tonnes per day of as-received lignite was assumed as the design basis in the study. Synthetic crude via direct liquefaction and pyrolysis and transportation fuels (gasoline, diesel and jet fuels) via indirect liquefaction were the product criteria for process prescreening. Production of pure methanol (99.5%) was included in the study as an alternative to indirect liquefaction. For comparative techno-economic evaluation of the selected processes the production of transportation fuels such as gasoline, diesel and jet fuels was considered for all the processes (except methanol plant) with the emphasis on maximization of gasoline production.

The major results of the study are presented in the paper.

**denotes speaker*

PRÉSENTATION 3

ÉTUDE SUR LA FAISABILITÉ TECHNIQUE ET ÉCONOMIQUE DE LA LIQUÉFACTION DU LIGNITE EN SASKATCHEWAN

J.A. Mikhlin, F.A. Ashraf et J.A. Dhawan*
SNC Inc.

RÉSUMÉ

L'étude a été faite par la SNC Inc., en 1981-1982, pour le compte de la Saskatchewan Oil and Gas Corporation (SASKOIL) et le Centre canadien de la technologie des minéraux et de l'énergie (CANMET). L'étude a compris un examen et une évaluation des procédés avancés de liquéfaction du charbon par les trois grands voies (liquéfaction directe, liquéfaction indirecte et pyrolyse) pour les lignites désignés de la Saskatchewan. L'évaluation des procédés de gazéfication du charbon, en voie d'élaboration (ou de commercialisation) aux États-Unis, en RFA et au RU, pour la production de gaz de synthèse à partir de lignites désignés (première étape de la liquéfaction indirecte), figurait également dans le mandat d'étude. L'évaluation préliminaire des procédés et des concepts de liquéfaction du charbon dont on envisage la commercialisation vers 1995, a également été faite.

Deux lignites de la Saskatchewan, i.e., Estevan et Willow Bunch, tels que reçus, ont été désignés comme charge d'alimentation (cendre: 15,4 wt % et 21,0 wt %, sur une base de lignite sec, respectivement; humidité 35 wt % pour les deux lignites). Dans l'étude, on n'a envisagé aucun prétraitement ou enrichissement des lignites.

L'évaluation technique, le pré-examen et l'attribution de la cote dans chaque voie, aux deux lignites Estevan et Willow Bunch, suivis par une évaluation techno-économique comparative de procédés choisis dans le cas du lignite désigné de Willow Bunch, ont été faits dans le cas des procédés avancés. Un procédé Fischer-Tropsch de type SASOL, commercialement éprouvé (Afrique du Sud), a également été envisagé à des fins de comparaison.

On a retenu comme base conceptuelle, pour l'étude, un tonnage quotidien de 25,000 tonnes de lignite tel que reçu. Le brut synthétique obtenu via la liquéfaction directe et la pyrolyse et les carburants de transport (essence, diesel et carburéacteurs) obtenus via la liquéfaction indirecte ont été les critères de produits retenus pour le préexamen du procédé. La production de méthanol pur (99,5 %) a été incluse dans l'étude comme une option de liquéfaction indirecte. Pour établir une évaluation techno-économique comparative des procédés choisis, la production des carburants comme l'essence, le diesel et le carburéacteur, a été envisagée pour tous les procédés (sauf dans le cas de l'usine de méthanol), en mettant l'accent sur la maximisation de la production d'essence.

La communication présente les principaux résultats de l'étude.

**indique le conférencier*

STUDY RELATING TO THE TECHNICAL AND ECONOMIC FEASIBILITY OF LIGNITE LIQUEFACTION IN SASKATCHEWAN

INTRODUCTION

A study relating to the technical and economic feasibility of lignite liquefaction in Saskatchewan was carried out by SNC Inc. during 1981-82 on behalf of Saskatchewan Oil and Gas Corporation (SASKOIL) and Canada Centre for Mineral and Energy Technology (CANMET). The study included review and assessment of coal liquefaction processes in application to two designated Saskatchewan lignites (Estevan and Willow Bunch) in all three major routes: direct liquefaction, indirect liquefaction, and pyrolysis (the last one may be considered as partial liquefaction). The study report comprises five volumes.

The processes evaluated were sub-divided into two categories:

1. Processes considered for commercialization by 1990.
2. Processes and concepts considered for commercialization around 1995.

The advanced processes selected by the Saskatchewan Coal Liquefaction Committee in the first category are presented in Table 1. Processes and concepts considered for commercialization around 1995 are listed in Table 2.

The evaluation of advanced processes (commercialization around 1990) was carried out in two stages. Stage I covered technical assessment, process pre-screening and ranking for both Estevan and Willow Bunch lignites. The objectives for Stage I were:

- updated technical review and evaluation of the processes
- prediction of liquefaction behaviour and suitability of Estevan and Willow Bunch lignites for the processes considered
- ranking and selection of the processes for technical and economic assessment (Stage II).

The objectives of Stage II included both technical and economic assessment of processes selected in Stage I for Willow Bunch lignite.

The scope of work in the second category (commercialization around 1995) was to review the state-of-the-art technology and ascertain the process applicability for Saskatchewan lignite as well as prospects for further development required.

In addition, an experimental program was carried out concurrently with the study to determine comparative reactivity of Estevan and Willow Bunch lignites. These tests were made by the Chemical Technology Division of B.C. Research.

In this presentation, the main emphasis is on advanced processes selected by the Saskatchewan Coal Liquefaction Committee for the study. Technical criteria for process pre-screening (Stage I) are discussed below.

As mentioned earlier, two Saskatchewan lignites from Estevan and Willow Bunch deposits as-received were designated as feedstocks for process pre-screening. Typical ultimate, proximate and petrographic analyses of the designated Estevan and Willow Bunch lignites are presented in Table 3. Both coals have high moisture and ash content. While the average moisture content is the same for both coals, the ash content of Willow Bunch lignite and inertinite content are higher. Also, both lignites have high oxygen and relatively low sulphur content. For conceptual design, plant size of 25,000 tonnes per day of as-received lignite was assumed. Synthetic crude (C_5-525°C) via direct coal liquefaction and pyrolysis were accepted as the desired products; for indirect liquefaction, transportation fuels such as gasoline, diesel, etc. were considered. For all cases, light hydrocarbon gases (C_1-C_4) were taken as co-products. For pyrolysis, char was also taken as a co-product. Other major process ranking criteria were:

- product yield and distribution
- product efficiency (overall and liquid)
- availability of process inputs (water, electricity, etc.)
- development status
- commercialization prospects and constraints.

Technical and economic criteria for Stage II of the study also included the following. For conceptual design, all processes were considered as grass-root facilities. The plant comprises a self-sufficient, integrated operation requiring coal, water and electricity as major raw material and process inputs. The as-received lignite supplied to the plant was assumed to be of similar composition as shown in Table 3. No pretreatment/beneficiation of coal to reduce moisture and ash (minerals) contents was considered. The desired products for both direct and indirect route were transportation fuels.

Preliminary or budget-type capital cost estimates, operating, maintenance and product cost evaluations were carried out for each of the selected coal liquefaction processes. All costs were calculated in *constant* mid-1982 Canadian dollars and no forward escalation beyond mid-1982 was included. Cost estimates and data received from process developers or licensers were used and these cost estimates were converted and adjusted to designated Saskatchewan locations. Product costs for pre-selected coal liquefaction processes are calculated using the methodology developed by the Engineering Society Commission on Energy Inc. (ESCOE) for comparisons and ranking of energy-related processes. Product costs were calculated on *Energy Value* and *Product Value* bases. The first method is based only on the heating value of the products whereas the second also considers the preferences and market value of the individual products. By-product credits were taken for sulphur, ammonia and mixed phenols.

ADVANCED DIRECT COAL LIQUEFACTION PROCESSES

A generalized typical block diagram of a self-sufficient, integrated, conceptual, commercial direct coal liquefaction plant is shown in Figure 1. The main processing areas are:

- coal preparation
- coal liquefaction
- gas treatment and light ends separation
- hydrogen production
- oxygen plant
- emission control
- effluent control
- utilities and offsites
- product storage and shipping (not shown).

Most of the process areas listed above, except coal liquefaction, have many common features for any of the processes considered. The coal liquefaction section is the most characteristic area for a specific process. Distinguishing features of the processes are highlighted below.

H-coal process: The process is a one-stage direct catalytic hydrogenation process. Dried and pulverized coal is mixed with recycled coal-derived oil and the coal-oil slurry is fed together with hydrogen into a high temperature and pressure ebullated-bed catalytic reactor (Co/Mo has been mostly used). In the reactor, the coal is liquefied at high temperature (425-455°C) and pressure (15-21 MPa) in the presence of hydrogen.

The reactor effluents leaving the top of the reactor are cooled and then separated into gases, liquids and residual slurry by conventional flash separation, fractionation and vacuum distillation techniques. Hydrocyclones have been used to separate the slurry into lean-solids and rich-solids streams prior to vacuum distillation.

The unique feature of the H-coal process is application of the commercially proven ebullated-bed reactor originally developed by HRI for the H-oil process to convert heavy oil residue into lighter fractions. The spent catalyst is periodically withdrawn and replaced by fresh catalyst through the on-line *addition and withdrawal* system.

RAG/Veba and Rheinbraun Processes: In these one-stage direct catalytic hydrogenation processes, a tubular up-flow reactor operating at high temperature and pressure is employed. Disposable red mud is added as a catalyst to the coal-oil slurry in the presence of molecular hydrogen.

Exxon Donor Solvent (EDS) Process: The main feature of this process is the role of the recycled solvent which donates hydrogen during coal liquefaction. Liquefaction of crushed coal is done in a non-catalytic tubular reactor in the presence of molecular hydrogen and hydrogen donor solvent. The donor solvent is a 205 to 545°C boiling range material which is hydrogenated in a separate, fixed-bed catalytic hydrogen reactor. The liquefaction reactor operates at 405 to 470°C temperature and 10.3 to 13.8 MPa pressure. The reactor effluents are separated by distillation into gaseous products, naphtha, distillates and vacuum bottoms slurry. The slurry is fed into the Flexicoking unit to recover additional distillate products. The coke is then gasified to produce syngas for hydrogen production. In this study, the EDS Design Update Case, which includes patented Flexicoking, was considered. Recent developments in the EDS process with bottoms recycle and gasification of remaining bottoms slurry for hydrogen production, etc., are evaluated in the later study on Onakawana lignite liquefaction.

Liquid Solvent Extraction (LSE) Process: The LSE process is a two-step process comprising an *extraction* stage where lignite is extracted with a solvent and the extract is separated from mineral matter and ash. The extraction reactor operates at a relatively low temperature and pressure (400°C and 2 MPa) and separation of solids is done by filtration to allow maximum recovery of coal-derived liquid (extract).

In the second *extract hydrogenation* stage, the coal-derived liquid hydrocracked at high pressure (20 MPa) and stabilized prior to fractionation.

Table 4 presents the typical reaction parameters, type of catalysts used, and hydrogen consumption for the direct coal liquefaction processes. All the processes, except LSE, employ more or less the same temperature (450-475°C). LSE (extraction stage) operates at a slightly lower temperature (400°C) and considerably lower pressure (2 MPa) compared with the H-coal and EDS processes (14-15 MPa) or the RAG/Veba and Rheinbraun processes (30 MPa).

The high operating severity required in the RAG/Veba or Rheinbraun processes is due to use of *low quality* but cheap and readily available red mud as a disposable catalyst (a waste clay obtained from processing of bauxite in aluminum production).

H-coal uses cobalt molybdate (American Cynamid, HDS-1442A) as a catalyst during coal liquefaction which is expensive but has better selectivity and hydrocracking activity. However, the *spent* catalyst must be periodically removed from the reactor (normally once a day) and replaced by fresh and/or regenerated catalyst through an on-line catalyst addition and withdrawal system. Results of catalyst regeneration and evaluation tests indicate that at best 80% to 90% of initial catalyst activity may be restored. Catalyst consumption is about 0.5 kg/t MF coal or 0.6 kg/t MAF coal processed and at this rate the annual requirement without regeneration will be approximately 2.6 Gg (2600 t). The supply of catalyst in such an amount is a concern, especially the availability of cobalt.

Table 5 presents the type of coals investigated extensively in the processes. A complete list of coals tested is presented in Volume II of the report. Bituminous and subbituminous coals have been tested in bench-scale, PDU, and demonstration pilot plants. However, in so far as low-rank coals are concerned, only EDS process has been tested on a larger scale (227-t/d pilot plant) using Texas lignite as a feedstock. Other processes have mainly been tested with the low-rank coals in bench-scale units only.

Estimated product yield and distribution for a conceptual commercial plant processing 25,000 t/d of designated Saskatchewan lignites is given in Table 6. For Willow Bunch lignite (21 wt % ash MF), only H-coal and LSE processes were considered since RAG/Veba, Rheinbraun, and EDS (Design Update Case) processes have low estimated liquid yield even with Estevan lignite containing 15.4 wt % ash MF.

For comparison of the processes on a consistent basis, the total liquid product yields and the desired liquid product (naphtha and mid-distillate) yield expressed in unit coal feed basis, i.e., bbl/t coal fed to the reactor and bbl/t coal supplied to the plant, are presented in Table 7. Product yield per tonne of coal supplied to the plant has been adjusted to zero electricity input for the RAG/Veba and EDS processes using the conversion factor of 10,000 Btu/kWh (10,550 kJ/kWh) and a fuel oil equivalent factor of 6 MM Btu/bbl (6.33 GJ/bbl).

Process Status

H-coal, EDS and RAG/Veba processes have been advanced to a pilot-plant scale (227-t/d H-coal plant at Catlettsburg, 227-t/d EDS plant at Baytown, and 200-t/d RAG/Veba plant at Bottrop).

The LSE process has been demonstrated on a continuous bench-scale installation having a capacity of processing 0.7-t/d (30 kg/h) of coal. Some of the process steps such as 2-t/d solvent extraction of coal and 0.7-t/d filtration unit have also been separately demonstrated in other installations.

The Rheinbraun process has been tested on a bench-scale unit of 0.25-t/d of coal only. Process design of a pilot plant (360-t/d of coal) was considered.

Process Ranking (Stage I of the Study)

The LSE process appeared to have the highest priority, especially for Willow Bunch lignite which was designated by the Study Committee as a feedstock for techno-economic assessment of preselected coal liquefaction processes (Stage II of the Study). The main concern in this respect is the development status of the LSE process, particularly due to the financial difficulties experienced by the process developer for continuation of the pilot-plant program.

The product yield, overall and liquid product efficiencies for the LSE process are higher than for the next competing H-coal process. The quality of primary products in the LSE process is also better and would require less upgrading to transportation fuels. The LSE process employs milder operating conditions during the extraction phase. Rapid deactivation of the catalyst in the H-coal process due to high ash content in Saskatchewan lignites could affect the catalyst regeneration efficiency and may lead to higher catalyst consumption. Also the two-step approach used in the LSE process offers operational advantages, in the sense that individual stages can be selectively optimized. Absence of mineral matter and ash in the hydrocracking stage (LSE process) prevents rapid deactivation of catalyst.

The third candidate appears to be the EDS process. It has lower product yields and efficiencies than LSE or H-coal but higher efficiencies than the RAG/Veba or the Rheinbraun processes. The EDS process has also been tested with high-ash content Texas lignite on a pilot-plant scale. If the ash content can be economically reduced by beneficiation/pretreatment to about 10 wt % MF coal, the one-step approach may be attractive.

New developments in H-coal (two-step concept) and EDS (bottoms recycle mode) processes should be considered in future work.

PYROLYSIS

The Lurgi-Ruhrgas (L-R) process is the advanced pyrolysis process selected by the Study Committee for evaluation of the designated Saskatchewan lignites.

The Lurgi-Ruhrgas (L-R) process is a flash carbonization process developed by Lurgi Kohle und fur Mineraloltechnik GmbH, in cooperation with Ruhrgas AG. The process has been used for carbonization of coals, oil shales, tar sands and asphaltic rocks. Cracking of hydrocarbons to produce olefins has also been tested.

The novelty of the L-R process is the use of hot, fine-grained product char as a heat carrier. Hot char is intimately mixed with the feed coal in a mechanical screw-mixer/carbonizer resulting in carbonization of the coal. Another essential feature is that char is simultaneously heated and pneumatically conveyed to the carbonizer, thus eliminating the need for a separate heater. The coal-to-char mixing ratio is kept between 4 and 8 to maintain the mixing temperature of approximately 600°C. The residence time in the mixer/carbonizer is kept very short to suppress secondary decomposition reactions and thus allow a higher liquid product yield.

Modified Fischer-Schrader Assay tests made by the Chemical Technology Division of B.C. Research indicated that low tar yields for Willow Bunch (Coronach) lignite (≈6-7 wt % MAF coal) and somewhat higher tar yields for Estevan lignite (≈9.5 wt % MAF coal) may be expected. Char yields for both lignites are high (64-66 wt % MAF coal). Therefore, in pyrolysis route, the Lurgi-Ruhrgas (L-R) process may be viable for Estevan lignite if a limited amount of liquid product is acceptable and surplus char can be marketed or utilized effectively in a power plant. For Willow Bunch lignite, the L-R process is not viable because of low predicted liquid product yields based on laboratory pyrolysis tests (Fischer-Schrader Assay). The L-R process was not considered for techno-economic assessment (Stage II of the Study).

INDIRECT COAL LIQUEFACTION

Indirect coal liquefaction, as distinguished from *direct* coal liquefaction (hydrogenation), involves gasification of the coal to produce synthesis gas ($CO + H_2$) as the first step, followed by conversion of the purified syngas to liquid hydrocarbons or to methanol in the subsequent steps. At present, there are three main process alternatives for the conversion of coal to liquid fuels via indirect coal liquefaction: Fischer-Tropsch synthesis, methanol synthesis and Mobil Methanol-to-Gasoline process. The following process alternatives in indirect coal liquefaction were selected by the Study Committee:

- SASOL-type plant with Fischer-Tropsch synthesis using Synthol reactor (F-T process)
- Coal-based Methanol-to-Gasoline plant with Mobil MTG process using fixed-bed reactor
- Coal-based plant for production of pure methanol (99.9% purity) as transportation fuel and/or blendstock for gasoline.

In order to determine the suitability of Saskatchewan lignites for liquefaction through an indirect route, emphasis was given to selection of an appropriate gasification process (including raw gas pretreatment required). After coal is converted into synthesis gas, any of the three process alternatives considered for the study may be technically feasible and the final overall process selection was made on the basis of the product yield and quality required, overall process economics, and readiness for commercialization.

For the gasifier evaluation, the following criteria were considered:

- – coal feed requirement (fines, moisture)
- – methane content in the raw gas
- – steam consumption
- – oxygen consumption
- – H_2/CO ratio in the product gas
- – operating pressure.

From the gasifiers evaluated (see Table 1), entrained-flow Koppers-Totzek gasifier appeared to have the highest priority for production of syngas from Saskatchewan lignite since the methane content in the gas produced is negligible and there are no restrictions on handling of coal fines. This gasifier is commercially proven on lignites with ash content up to 32 wt % MF coal.

The second-generation fluidized-bed gasifiers, High-Temperature Winkler (HTW) and Westinghouse, appear to be next best for gasification of Saskatchewan lignites. Experimental tests required by process developer to confirm the gasification behaviour of Saskatchewan lignites were beyond the scope of the study. Based on the experimental results, a techno-economic comparison of these gasifiers' configuration with entrained-flow K-T gasifier was recommended.

TECHNO-ECONOMIC ASSESSMENT OF PRE-SELECTED PROCESSES (STAGE II OF THE STUDY)

In Stage II, techno-economic assessment was carried out for pre-selected processes, i.e., LSE in the direct coal liquefaction route and three process alternatives in the indirect coal liquefaction route (methanol plant, Mobil MTG plant and SASOL-type plant) with Koppers-Totzek gasifier for production of synthesis gas. For consistent comparison of direct and indirect coal liquefaction routes, the transportation fuels such as gasoline, diesel and jet fuel with emphasis on the production of gasoline are considered for all cases (except methanol plant). Other technical and economic criteria applied were presented earlier.

A summary of techno-economic results is shown in Table 8. For LSE process, two cases representing the lower (65% on MAF basis) and upper extraction levels (82% MAF basis) are presented.

Analyzing the product output and distribution, it may be seen that different products in varying amounts are produced in the processes. However, all the products meet the standard liquid fuel specifications. Comparison of the total amount of desired liquid products (gasoline, jet fuel, diesel and fuel oil) shows that the LSE process has the highest yield (4154 to 4387 t/d) followed by Mobil MTG (2245 t/d). The lowest yield is for SASOL-type F-T plant (1332 t/d). However, all the liquid produced in Mobil MTG is gasoline while in the LSE process 36 wt % is gasoline, 34 wt % jet fuel and the remaining 30 wt % is diesel fuel. The product yield from the methanol plant is not compared with other processes because of the different nature of the product.

The total product yield is highest for the LSE process, followed by Mobil MTG, and the lowest for SASOL-type F-T plant. Similar trends are observed in overall and liquid product efficiencies*.

The total capital investment for a self-sufficient, integrated plant processing 25,000 t/d of as-received Willow Bunch lignite is nearly the same for LSE and SASOL-type F-T plants and is lowest for Mobil MTG plant. However, investment per daily production of desired products is lowest for LSE, followed by Mobil MTG and F-T plants. In other words, a plant based on equal output of products would have the lowest capital investment for the LSE process and highest capital investment for F-T plant. If gasoline was the only desired product, the capital investment per daily production of gasoline would be by far the lowest for Mobil MTG plant.

The product costs for LSE and Mobil MTG process are nearly the same but for the SASOL-type plant it is quite high. However, the breakdown of product cost into main components shows that they are of the same proportion in all cases.

**In this study, a modified version of thermal efficiency widely used in the energy-related process is employed. The modified definition of the efficiency is the total gross-calorific-value (GCV) of all the products divided by the total input energy of the lignite feed and electric power.*

The status of the LSE process was discussed earlier. The development status is a main concern. The Mobil MTG process has better commercialization prospects since the only part of this process that was not demonstrated commercially is the methanol-to-gasoline conversion step. The SASOL-type F-T plants are commercially proven. The SASOL-type plant, although commercially proven, has very low desired product yield and is expensive.

For the methanol plant, the product yield is 2.69 bbl/t MF coal whereas the product efficiency is relatively low (about 39%), primarily due to the indirect method of liquefaction. Capital costs are relatively lower and the product costs are comparable to present market prices (which are based on the use of methanol as chemical feedstock only). The disadvantages are that methanol has low energy content and several practical problems are associated with its use as a fuel, such as uncertain market demand, distribution and storage difficulties, cold starting problems, lower tolerance for water, etc.

PRELIMINARY EVALUATION OF NEW PROCESSES OR CONCEPTS

In addition to assessment of advanced direct and indirect coal liquefaction and pyrolysis processes, a preliminary review of new processes or concepts listed in Table 2 was carried out to determine the state-of-the-art, demonstration scale and R&D status, including funding available. A summary is presented in Table 9. While some of the processing steps and features are attractive, process development work has been abandoned in most cases due to financial constraints. In view of the slowdown and present oil glut in the world, the prospects for commercialization of these processes around 1995 are uncertain.

The coprocessing option has potential merits, especially for the Province of Saskatchewan where lignite and heavy oil are available. However, at the time of the study, the development work was on the autoclave/bench-scale level. Further R&D work was recommended.

TABLES

Table 1 – Processes selected by the Saskatchewan Coal Liquefaction Committee and considered for commercialization by 1990

Process	Process developer (licenser)	Country
	Direct coal liquefaction	
H-coal	Hydrocarbon Research Inc.	U.S.A.
RAG/Veba	Ruhrkohle AG and Veba Oel AG	F.R.G.
Rheinbraun	Rheinische Braunkohlenwerke AG	F.R.G.
Exxon donor solvent (EDS)	Exxon Research and Engineering Company	U.S.A.
Liquid solvent extraction (LSE)	National Coal Board, Coal Research Establishment	U.K.
	Coal pyrolysis	
Lurgi-Ruhrgas	Lurgi Mineraloltechnik GmbH and Ruhrgas AG	F.R.G.
	Indirect coal liquefaction	
SASOL-type Fischer-Tropsch	SASOL Ltd.	South Africa
Mobil Methanol-to-Gasoline (M-MTG)	Mobil Research and Development Corporation	U.S.A.
	Gasifiers for Production of Synthesis Gas	
Lurgi (dry bottom)	Lurgi Mineraloltechnik AG	F.R.G.
British Gas/Lurgi (slagging)	British Gas Corporation and Lurgi Mineraloltechnik AG	U.K. F.R.G.
Koppers-Totzek	Krupp-Koppers GmbH	F.R.G.
Texaco	Texaco Research and Development Corporation	U.S.A.
Winkler (high temperature)	Rheinische Braunkohlenwerke AG	F.R.G.
Westinghouse	Westinghouse Electric Corporation	U.S.A.

Table 2 – Processes and concepts selected by the Saskatchewan Coal Liquefaction Committee and considered for commercialization around 1995

Process	Process developer (licenser)	Country
	Direct coal liquefaction	
Zinc halide	Consolidation Coal Co.	U.S.A.
Dow coal liquefaction	Dow Chemicals Co.	U.S.A.
Consol synthetic fuel (CFF)	Consolidation Coal Co.	U.S.A.
Solvent refined coal (SRC-1)	International Coal Refining Co.	U.S.A.
Solvent refined lignite (SRL)	University of North Dakota	U.S.A.
CO-steam	Grand Forks Energy Technology Center	U.S.A.
Two-step liquefaction	Cities Service Co. C-E Lummus Co.	U.S.A.
	Coal pyrolysis	
Occidental Pyrolysis	Occidental Research Corporation	U.S.A.
	Indirect coal liquefaction	
	Gasifiers for production of synthesis gas	
Shell gasifier	Shell International Petroleum	The Netherlands
U-gas	Institute of Gas Technology	U.S.A.
	Coprocessing	
Coil	Hydrocarbon Research Inc.	U.S.A.
Solvolysis	Mitsubishi Heavy Industries Ltd.	Japan

Table 3 – Typical ultimate, proximate, and petrographic analysis of Saskatchewan lignites

	Estevan	Willow Bunch***
Moisture (as received), wt %	35.0	35.0
Gross calorific value (GCV)	24 270	20 270
Proximate analysis, wt % MF coal		
Volatile matter	42.0	39.6
Fixed carbon	42.2	38.5
Ash	15.4	21.0
Sulphur	0.6	0.9
Ultimate analysis, wt % MF coal		
Carbon	61.2	52.1
Hydrogen	4.5	4.0
Nitrogen	1.0	0.5
Sulphur	0.6	0.9
Oxygen	17.3	21.5
Ash	15.4	21.0
Petrographic analysis, vol %		
Vitrinite*	81.2	77.6
Exinite	7.9	1.7
Inertinite	9.9	18.7
Mineral matter	0.9	2.0
Ash analysis, wt %		
Silica, SiO_2	47.1	42.1
Alumina, Al_2O_3	17.8	15.6
Titania, TiO_2	**	0.9
Ferric oxide, Fe_2O_3	2.5	6.7
Lime, CaO	11.7	14.3
Magnesia, MgO	2.9	5.0
Potassium oxide, K_2O	0.5	1.3
Sodium oxide, Na_2O	5.0	1.8
Phosphorus pentoxide, P_2O_5	1.0	
Sulphur trioxide, SO_3	1.0	
Undetermined	10.5	12.3

* *Equivalent to huminite in low-rank coals*

** *Undetermined*

*** *Particle size distribution shows that up to 25% of crushed coal is fines*

Source: *Letter to Dr. F.M. Mourits, Coal Liquefaction Study Management, Saskoil, dated December 15, 1981, to Dr. J.A. Mikhlin, SNC Inc.*

Table 4 – Typical reaction parameters of advanced direct coal liquefaction processes

	H-coal	RAG/Veba	Rheinbraun	EDS	LSE
Temperature, °C	455	475	460	450	400 *
Pressure, MPa	15.5	30.0	30.0	14.0	2.0*
Catalyst used – Type	Co/Mo (HDS-1442A)	Red mud (34% Fe_2O_3)	Red mud (34% Fe_2O_3)	Co/Mo	Co/Mo
– Amount, kg/t MAF coal	0.6	65 (22)	50 (17.5)	N/A#	0.06##
Space velocity, kg/h/m³	480	530	590	750	N/A
Oil/coal ratio	1.2	1.8	1.3	1.6	2.0
Hydrogen consumption kg/100 kg MAF coal	6.8	6.3	6.0	4.4**	0.0*

# Not available, but the consumption would be in the range of 0.05 to 0.1 kg/t MAF coal

## Catalyst consumption has been estimated assuming replacement every two years

** Conditions reported for first stage. For second stage, pressure in hydrocracking operating is 20 MPa, temperature about 450°C, and H_2 consumption is in the range of 5.0 to 6.5 kg/100 kg MAF coal*

*** Refers to design update case; the total hydrogen consumption including solvent hydrogenation is 5.7 to 6.3 kg/100 kg MAF coal*

Table 5 – Types of coals* tested in advanced direct coal liquefaction processes

	H-coal	RAG/Veba	Rheinbraun	EDS	LSE
Bituminous	Illinois No. 6 Kentucky No. 9	Ruhr coal	–	Illinois No. 6	U.K. coal (CRC-702)
Subbituminous	Wyodak	–	–	Wyodak Wandoan	
Lignite/Brown	Texas North Dakota Australian Brown		Rhenish Brown	Texas North Dakota	Australian Brown

** Coals that were tested briefly or only in preliminary tests are not included. A complete list of coals tested is covered in the detailed technical review given in Volume II of the report*

Table 6 – Product yields and distribution (Basis: 25,000 t/d of lignite to the plant)

	Estevan lignite					Willow Bunch lignite		
Processes	H-coal	RAG/Veba	Rheinbraun	EDS	LSE**	H-coal	LSE*	LSE**
MF coal, T/D								
– to Reactor	16 250	12 505	10 860	15 625	11 640	14 428	14 152	11 640
– for fuel gas and make-up H_2 production	–	–	1 555	–	3 925	–	1 267	3 926
– to utilities	–	3 745	3 835	625	665	1 822	831	684
Electricity from outside source, MW	–	160	–	110	–	–	–	–
Gaseous products, T/D								
– propane/butane	132	952	592	322	495	–	469	447
Liquid products, T/D								
– Naphtha	2 327	1 058	1 323	2 210	1 770	1 420	1 390	1 457
– Mid-distillate	2 000	3 553	2 397	2 746 }	3 049	1 660	2 780	2 926
– Heavy oil	865	–	–	–	–	286	–	–
Byproducts, T/D								
– Sulphur	145	57	56	84	87	142	125	125
– Ammonia	87	116	76	114	76	88	64	64
– Phenols	17	–	–	–	–	20	32	32

* *65% extraction on MAF based on experimental test with a Willow Bunch lignite*

** *82% extraction on MAF based on preliminary prediction by process developer by comparison of typical analysis of Saskatchewan lignites with other similar coals tested in LSE process*

Table 7 – Product yield and efficiency of advanced direct coal liquefaction processes

Coal	Estevan lignite					Willow Bunch lignite		
Processes	H-coal	RAG/Veba	Rheinbraun	EDS	LSE**	H-coal	LSE*	LSE**
Percentage of total coal fed to reactor	100	77	67	96	72	89	87	72
Total liquid product yield								
bbl/t as-received coal to reactor	1.52	1.57	1.64	1.42	1.79	1.11	1.19	1.51
bbl/t MF coal to reactor	2.34	2.41	2.52	2.19	2.75	1.71	1.83	2.33
bbl/t MAF coal to reactor	2.76	2.85	2.98	2.59	3.25	2.17	2.32	2.95
Adjusted total liquid product Yield #								
bbl/t as-received coal to plant	1.52	0.95	1.10	1.19	1.29	0.99	1.03	1.09
bbl/t MF coal to plant	2.34	1.47	1.69	1.83	1.98	1.52	1.59	1.68
bbl/t MAF coal to plant	2.76	1.73	2.00	2.16	2.34	1.93	2.02	2.12
Adjusted total liquid product Yield including LPG ##								
bbl/t as-received coal to plant	1.56	1.25	1.28	1.29	1.43	0.99	1.17	1.22
bbl/t MF coal to plant	2.40	1.92	1.97	1.99	2.20	1.52	1.80	1.87
bbl/t MAF coal to plant	2.84	2.27	2.33	2.35	2.60	1.93	2.28	2.37
Adjusted desired liquid product Yield (Naphtha and mid-distillate)								
bbl/t as-received coal to plant	1.29	0.95	1.10	1.03	1.29	0.92	1.03	1.09
bbl/t MF coal to plant	1.99	1.47	1.69	1.58	1.98	1.41	1.59	1.68
bbl/t MAF coal to plant	2.36	1.73	2.00	1.87	2.34	1.79	2.02	2.12
Product efficiency								
Overall	62.0	55.7	52.2	53.4	62.0	46.8	58.9	61.2
Total liquid product (excluding LPG)	59.0	44.0	43.2	48.2	55.0	45.7	51.4	54.0
Desired liquid product	49.7	44.0	43.2	35.4	55.0	45.7	51.4	54.0

# For RAG/Veba and EDS processes, the yields in bbl/t coal to plant have been adjusted to zero electricity import using 10,000 Btu/kWh (10,550 kJ/kWh) and fuel oil equivalent factor of 6 MM Btu/bbl (6.33 GJ/bbl)

## For LPG produced in the processes, the number of barrels has been added using fuel oil equivalent factor of 6 MM Btu/bbl (6.33 GJ/bbl)

** Represents product yields for 65% extraction on MAF basis*

*** Represents product yields for 82% extraction on MAF basis*

Table 8 – Summary of techno-economic assessment

		LSE process		Mobil MTG plant	SASOL-type F-T plant	Methanol Plant
		65% extraction MAF basis	82% extraction MAF basis			
Product output and distribution, t/d						
Fuel gas		–	–	64	784	–
Propane		–	–	117	69	–
Propane/butane (LPG)		389	410	–	–	–
Butane		–	–	186	11	–
Heavy fuel oil		–	–	–	63	–
Jet fuel		1 402	1 481	–	–	–
Diesel		1 262	1 334	–	214	–
Gasoline		1 490	1 572	2 245	1 055	–
Mixed alcohols		–	–	–	133	–
Methanol		–	–	–	–	5 714
Desired liquid product yield*						
bbl/t as-received coal to plant		1.11	1.17	0.77	0.46	1.75
bbl/t MF coal to plant		1.71	1.80	1.19	0.71	2.69
bbl/t MAF coal to plant		2.16	2.27	1.50	0.91	3.41
Total product yield**						
bbl/t as-received coal to plant		1.12	1.19	0.94	0.94	1.75
bbl/t MF coal to plant		1.73	1.83	1.45	1.44	2.69
bbl/t MAF coal to plant		2.19	2.32	1.84	1.82	3.41
Product efficiency						
Desired liquid product		51.0	54.0	31.4	18.0	–
Total liquid product		51.0	54.0	31.4	18.9	39.1
Overall product		57.5	60.7	43.5	36.0	39.5
Capital investment, $ million		2 639	2 639	2 213	2 545	1 926
Investment, $/daily bbl of desired liquid product*		95 054	90 000	114 750	219 245	44 010
Investment, $/daily bbl of total products**		93 740	88 765	93 770	109 035	44 010
Average product cost, $/10^{6}kJ						
Energy value basis		9.48	8.97	11.28	15.27	11.14
Product value basis		12.43	11.76	13.92	22.72	8.70
Individual product cost (product value basis)						
Fuel gas	$/10^{6}kJ	–	–	4.87	7.95	–
Propane	$/bbl	–	–	22.37	36.61	–
Propane/butane	$/bbl	22.03	20.84	–	–	–
Butane	$/bbl	–	–	35.64	62.45	–
Heavy fuel oil	c/L	–	–	–	83.54	–
Jet fuel	c/L	29.3	27.7	–	–	–
Diesel	c/L	41.1	38.9	–	66.1	–
Gasoline	c/L	43.6	41.2	45.3	72.7	–
Mixed alcohols	c/bbl	–	–	–	86.4	–
Methanol	$/bbl	–	–	–	–	32.97
Components of product cost, %						
Coal cost		13.8	13.8	15.1	13.4	16.9
Operating and maintenance cost		32.6	32.6	34.1	34.9	33.8
Capital cost		53.6	53.6	50.8	51.7	49.3

* *Desired liquid products are gasoline, diesel, jet fuel (pure methanol in methanol plant)*

** *Total product refers to all the products listed above*

Table 9 – Process demonstration scale and status of new processes or concepts considered for commercialization around 1995

Process	Demonstration scale	R&D status	Funding status
Direct coal liquefaction (one-stage hydrogenation)			
– Dow	0.1 t/d	In progress (till Dec. 82)	Current (till Dec. 82)
– CO-steam	2.3 kg/h (Dismantled)	Abandoned	None
Direct coal liquefaction (two-stage hydrogenation)			
– Consol Synthetic Fuel (CSF)	9.0 t/d (Dismantled)	Abandoned	None
– Two-stage liquefaction (TSL)	0.5 t/d	In progress	Current (till Dec. 82)
– Solvent-refined coal (SRC)	45 t/d	Demo. plant Eng. Design In progress	Current (till Dec. 82)
– Zinc halide (Z-H)	1.0 t/d	Abandoned	None
– Solvent-refined lignite (SRL)	0.5 t/d (Dismantled)	Abandoned	None
Indirect coal liquefaction (gasification processes)			
– Shell	150 t/d	In progress	Not determined
– U-gas	25 t/d	In progress	Not determined
Coal-oil coprocessing			
– Coil	30 bbl/d	Abandoned	None
– Japanese solvolysis coal liquefaction (JSCL)	1.0 t/d	In progress	Not determined
– Veba coal/oil process	Auto-clave	In progress	Not determined
Pyrolysis			
– Occidental	2.5 t/d	Abandoned	None

FIGURE

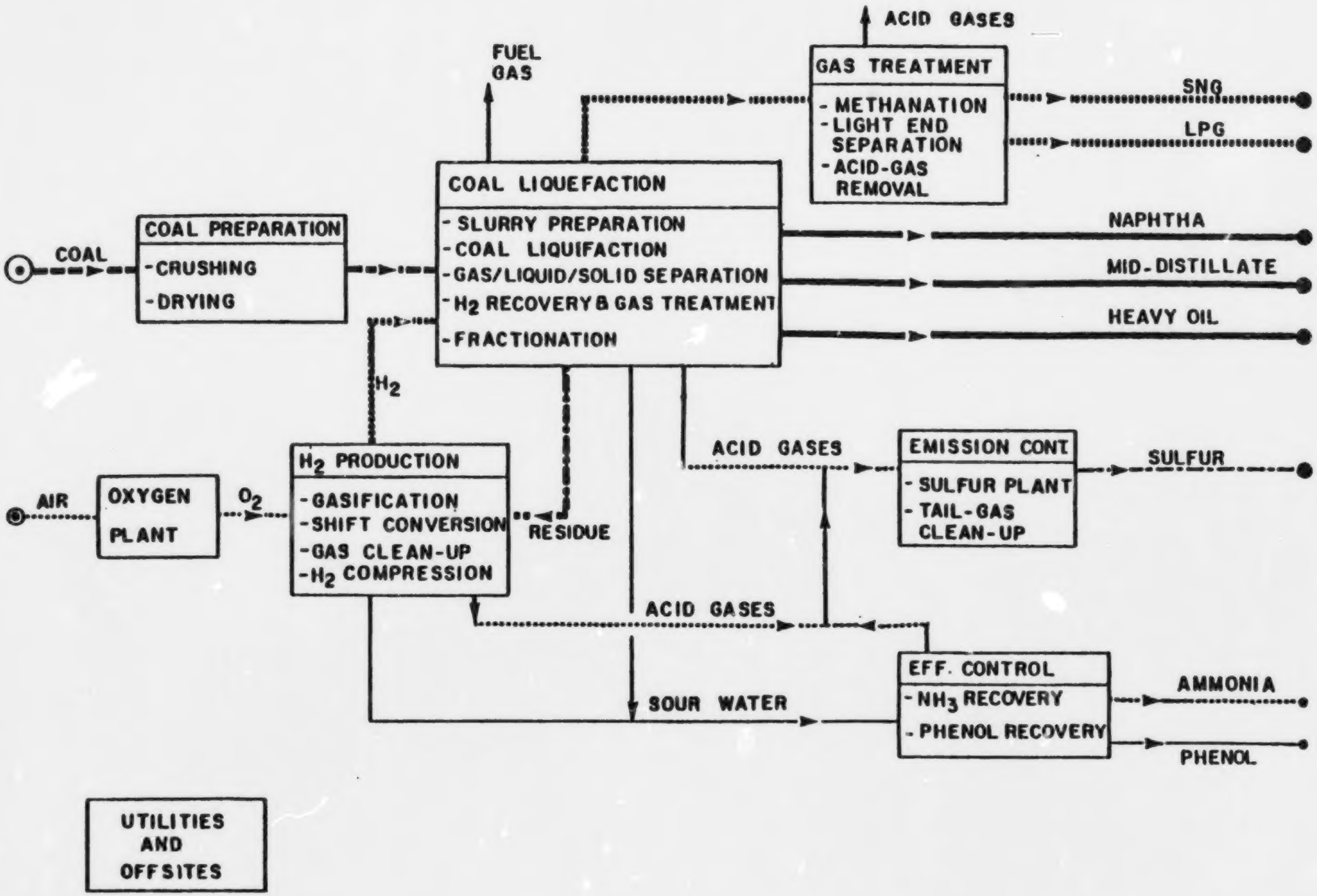

ACID GASES
FUEL GAS
GAS TREATMENT
- METHANATION
- LIGHT END SEPARATION
- ACID-GAS REMOVAL
SNG
LPG
COAL LIQUEFACTION
- SLURRY PREPARATION
- COAL LIQUIFACTION
- GAS/LIQUID/SOLID SEPARATION
- H_2 RECOVERY & GAS TREATMENT
- FRACTIONATION
COAL
COAL PREPARATION
- CRUSHING
- DRYING
NAPHTHA
MID-DISTILLATE
HEAVY OIL
H_2
ACID GASES
EMISSION CONT.
- SULFUR PLANT
- TAIL-GAS CLEAN-UP
SULFUR
AIR
OXYGEN PLANT
O_2
H_2 PRODUCTION
- GASIFICATION
- SHIFT CONVERSION
- GAS CLEAN-UP
- H_2 COMPRESSION
RESIDUE
ACID GASES
EFF. CONTROL
- NH_3 RECOVERY
- PHENOL RECOVERY
AMMONIA
PHENOL
SOUR WATER
UTILITIES AND OFFSITES

Fig. 1 – Typical block diagram of integrated coal liquefaction commercial plant

SESSION I: PAPER 4

AN ASSESSMENT OF TECHNOLOGIES FOR THE DIRECT LIQUEFACTION OF ONAKAWANA LIGNITE

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Dr. J. Mikhlin &
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ABSTRACT

Lignite, found in the Onakawana area of northeastern Ontario, is a low-rank, high-ash coal. The Onakawana deposit is estimated to contain approximately 170 million tonnes.

In October 1982, the Ontario Ministry of Energy awarded a contract to S.N.C. to carry out an assessment of technologies for the direct liquefaction of Onakawana lignite. The assessment was divided into three phases.

Results of Phase I and Phase IIA are presented as well as preliminary data on Phase IIB.

**denotes speaker*

PRÉSENTATION 4

UNE ÉVALUATION DES TECHNIQUES DE LIQUÉFACTION DIRECTE DU LIGNITE D'ONAKAWANA

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RÉSUMÉ

Le lignite de la région d'Onakawana, dans le nord-est de l'Ontario, est un charbon à forte teneur en cendre de faible rang. On a estimé que le gisement d'Onakawana renferme quelque 170 millions de tonnes.

En octobre 1982, le ministère d'État à l'Énergie confiait par contrat à la S.N.C. le mandat d'établir une évaluation des technologies susceptibles d'assurer la liquéfaction directe de ce lignite. L'évaluation a été faite en trois phases. Le rapport présente les resultats de la Phase I et de la Phase IIA de même que les données préliminaires de la Phase IIB.

Les résultats de la Phase I et de la Phase IIA sont présentés et certaines données préliminaires concernant la Phase IIB de l'étude sont discutées.

**indique le conférencier*

AN ASSESSMENT OF TECHNOLOGIES FOR THE DIRECT LIQUEFACTION OF ONAKAWANA LIGNITE

INTRODUCTION

In 1979, The Ontario Ministry of Energy issued a document entitled "Energy Security for the Eighties: A Policy for Ontario". This document identified security of crude oil supply as Canada's, and Ontario's, primary concern. The province recognized that this potential problem could be minimized by the use of its indigenous energy resources. Lignite, Ontario's only known coal deposit, could serve this purpose by being converted to synthetic crude oil.

Slide 1

These deposits are in the James Bay Lowlands in northern Ontario. Onakawana, where the lignite was first discovered, is located alongside the Ontario Northland Railway tracks, about 100 km south of Moosonee and 200 km north of Cochrane. The deposit is estimated to contain 170 million tonnes of lignite. Recently, the Ontario Energy Corporation completed a three-year drilling program west of the Onakawana deposit and estimated that there were potential additional resources of 700 million tonnes.

In 1982, the Ministry of Energy commissioned an assessment of the technologies for the direct liquefaction of Onakawana Lignite. This study was divided into three phases:

Phase I

Phase I is a preliminary evaluation of the Onakawana lignite as feedstock for direct liquefaction, including a detailed laboratory assessment of the fundamental analytical properties such as ultimate, proximate and petrographic analyses.

Phase II

Phase II is a technology assessment and prescreening of processes for the as-received (high-ash) Onakawana lignite. It was divided into two sub-phases:

1. In Phase IIA, the as-received lignite (ash content 19.5 wt % on a moisture-free lignite basis) was considered as a feedstock.
2. In Phase IIB, the beneficiated lignite having reduced ash content (around 10 wt % on a moisture free lignite basis) is considered as a feedstock.

A novel concept of coal beneficiation as an integral part of a direct liquefaction process, proposed by Mikhlin (1983), was incorporated in Phase IIB.

The design calculations are based on experimental data obtained with Onakawana lignite samples in the program on beneficiation of low rank coals using the above concept. The program is funded by CANMET.

Phase III

Phase III is a techno-economic evaluation of the best direct liquefaction process selected as the most suitable for Onakawana lignite.

At present, Phase I and Phase IIA are completed. The work of Phase IIB of the study is still being carried out. Therefore, only some Phase IIB data available will be discussed.

DISCUSSION AND PRELIMINARY RESULTS

Phase I

It was decided, at the start of the study, not to undertake expensive drilling at the Onakawana site. Instead, an assessment took place using the remainder of the lignite which had been taken from a test pit for a study conducted in 1980.

It was necessary to ensure that the sample of the lignite used for analyses was representative of the lignite deposit. Proximate, ultimate and petrographic analyses of this sample were carried out and results compared with the *representative* quality of the Onakawana deposit. The representative quality of the deposit was determined through statistical evaluation of the lignite analyses obtained in the course of drillings carried out in 1972 and 1980.

Typical analyses of Onakawana lignite are shown in the next slide.

Slide 2

Onakawana lignite as-received has high ash and moisture content which would adversely affect the net liquid product yield, efficiency and overall economics of a coal liquefaction plant.

The ash is disseminated to a very fine state. Therefore, reduction of ash content by conventional gravity separation is not sufficient to warrant the loss of lignite and the cost of the process, as it was confirmed by a sink-float test of Onakawana lignite made by the Ontario Research Foundation.

Phase II

The following four direct liquefaction processes have been selected for technology assessment and prescreening:

Process	*Developer*
Exxon donor solvent (EDS)	Exxon Research & Engineering Company, U.S.A.
Liquid solvent extraction (LSE)	National Coal Board, U.K.
H-coal	Hydrocarbon Research, Inc., U.S.A.
RAG/VEBA	Ruhrkohle AG and Veba Oel Ag, F.R.G.

Technology evaluations of the above processes were carried out in the study of the technical and economic feasibility of lignite liquefaction in Saskatchewan, discussed in the previous paper. However, during the past three years these processes have been improved through ongoing research and development carried out by the process developers. The most recent developments and data available on each of these processes have been taken into account in the current study. Also, the liquefaction test carried out with Onakawana lignite by the National Coal Board, U.K. (developer of LSE process), revealed that this lignite has higher reactivity (conversion to liquid and gases without use of catalyst or hydrogen is about 87-90 wt % vs about 65 wt % MAF for Willow Bunch Saskatchewan lignite at similar conditions).

In light of recent developments in the above processes and the NCB test results, the EDS process in bottoms recycle mode of operation and the LSE process have a potential for relatively more economic liquefaction of as-received high ash Onakawana lignite as compared to other direct liquefaction processes considered.

EDS is a one-step, non-catalytic direct hydroliquefaction process in which hydrogen donor solvent is mixed with feed coal and the coal-oil slurry is fed to the liquefaction reactor. In the bottoms recycle mode of operation, a portion of the vacuum bottoms residue is also recycled to the liquefaction reactor. According to the EDS process developer's data, the conversion of high ash lignite to liquid products sufficiently increases at a high ratio of recycled bottoms residue to feed lignite (about 1.0). This phenomenon was demonstrated in a 227 metric tons per day EDS coal liquefaction plant in Baytown, Texas using high ash Texas lignite as a feedstock.

LSE is a two-stage process. The first stage includes coal extraction followed by solids separation from the extract. The second stage entails catalytic hydrocracking of the solids-free extract. Filtration is used for separation of solids (ash and unreacted coal). This allows the disposal of solids with much lower losses of liquid products in comparison to other coal liquefaction processes where non-mechanical, liquid-solid separation techniques are used (e.g., vacuum distillation, etc.).

Thus, the EDS process in bottoms recycle mode of operation and the LSE process were selected for technology assessment using as-received (high ash) Onakawana lignite as a feedstock (Phase IIA of the study).

Selection of an appropriate process configuration and solid-liquid separation method is one of the ways to reduce negative influence of high ash content in the feed coal. However, the most radical approach is to reduce ash content in the coal prior to its liquefaction, i.e., by beneficiating the coal. A technology assessment of all four processes listed above, using beneficiated Onakawana lignite, was included in Phase IIB of the study.

As previously mentioned, conventional beneficiation by washing is not acceptable economically for Onakawana lignite due to dissemination of ash in the lignite to a fine state. A novel concept of coal beneficiation as an integral part of the direct liquefaction process proposed by Mikhlin (1983) was incorporated in Phase IIB of the study.

According to the suggested concept, a portion of the oil (or combination of oils) used for coal-slurry preparation in a coal beneficiation plant will first be applied to beneficiation of the ground high ash coal and then proceed with cleaned coal particles as agglomerates directly to preparation of the coal-oil slurry to be fed into the liquefaction reactor. This way, generally, the coal grinding and oil costs for beneficiation may mostly be written off from the product cost of the technological complex comprising integrated direct liquefaction and beneficiation plants, while the net liquid product yields and overall efficiency and economics of the complex would be substantially improved due to processing beneficiated coal having reduced ash content.

The preferential wetting and agglomeration of coal by oil is based on differences in surface properties of ash forming (usually hydrophilic) and carbonaceous constituents (which should be hydrophobic or at least less hydrophilic than ash constituents). A decrease in rank from bituminous coal to subbituminous to lignite is usually associated with a gradually less hydrophobic (more hydrophilic) balance of the coal surface properties. However, experimental research being conducted by SNC has given promising results with low rank coals using model coal derived oils and chemicals. Tests carried out with Onakawana lignite resulted in up to 70% reduction of ash with recovery of carbonaceous constituents up to 95-98 wt % at definite conditions.

The next slide presents a generalized block diagram of a conceptual commercial plant for integrated beneficiation and direct liquefaction of Onakawana lignite.

Slide 3

Apart from the beneficiation section, the plant comprises generally the same major processing areas as it does for non-beneficiated (as-received) lignite. However, some adjustments and modifications of parameters, configuration and design have to be made to facilitate recovery of coal-derived oils and chemicals suitable also for beneficiation of low rank coals, thus forming a novel integrated beneficiation-liquefaction technological complex based on known coal liquefaction technologies. The major plant areas are coal preparation, coal liquefaction, gas treatment and light end separation, hydrogen production, emission and effluent control, utilities and offsites.

In the case of processing non-beneficiated Onakawana lignite, the lignite received at the plant-site after primary and secondary crushing with about 20 wt % ash MF and 35 wt % equilibrium moisture, is pulverized and simultaneously pre-dried. Pulverized, partially dried lignite is mixed with recycled oil, dried in slurry to about 4% moisture, pre-heated and fed to a liquefaction reactor. Reactor effluent stream is treated in gas-liquid-slurry separation units to recover gaseous and liquid products and separate unreacted lignite and ash. Excess hydrogen is also recovered and recycled to the liquefaction reactor. The separated solids (ash and unreacted lignite) are gasified to produce make-up hydrogen. Product liquids are upgraded to obtain stabilized naphtha, middle distillate and propane-butane LPG. Effluents treatment and emission control limit the discharge of pollutants. By-products such as sulphur, ammonia, and phenols are recovered.

In the case of beneficiation (reduction of ash content) of lignite as an integral part of liquefaction, the pulverized and partially dried lignite and a portion of recycled oils are fed to the beneficiation section. The agglomerates containing lignite with reduced ash content are conveyed from the beneficiation section to the coal-slurry preparation units being pre-dried at the same time to about 20 wt % moisture. Further processing of coal-oil slurry is similar for liquefaction in both the non-beneficiated (as-received) and beneficiated lignite cases. The lignite rejects in beneficiation tailings are separated and used for production of fuel gas or hydrogen make-up in the gasification section.

Some specific features of the EDS Bottoms Recycle and LSE processes have been discussed earlier. The major features of H-coal and RAG/Veba processes were presented in the previous paper.

Technical and economic criteria for Phase II of the study are shown in the next slide.

Slide 4

Technology assessment includes detailed technical evaluation of the processes and cost considerations. The emphasis in the technical evaluation of the processes is on liquefaction of lignites, process models for lignites, design studies of conceptual commercial plants which have been prepared by the corresponding process developers, as well as on process status and commercialization prospects. For each of the processes, overall configuration of a conceptual commercial plant for liquefaction of Onakawana lignite was developed. Product yield and distribution, overall and liquid product efficiencies, quality and possible utilization of the products for substituting conventional fuels (gasoline, diesel and jet fuel) are included. The technology assessment in Phase II of the study was carried out using the data on liquefaction behaviour of the coals tested by corresponding process developers and analytical properties of Onakawana lignite.

For the LSE process, as previously mentioned, a liquefaction test with Onakawana lignite was also carried out.

Cost considerations are based on the methodology for process prescreening cost estimation developed by SNC. The methodology establishes a consistent basis for cost estimates in spite of differences in cost estimation philosophy, methodology and bases used by different process developers.

The cost considerations include estimates of capital investment, operating, maintenance and product costs for each of the processes. The capital investment calculations are based on the direct equipment costs reported by the process developers per vendors' quotations. These are the most reliable parts of different process developers' estimates. The most recent cost estimates obtained from the process developers, which reflect their experience gained through operation of demonstration pilot plants, were considered. For the beneficiation section, where appropriate, preliminary quotations obtained directly from equipment vendors were taken into account. The indirect cost and other components of capital investment are calculated by taking relevant cost factors developed by Statistics Canada for construction of capital intensive petrochemical plants.

The product costs are calculated using the methodology developed by the Engineering Societies Commission on Energy Inc. (ESCOE) for cost comparisons of energy projects which take into account both the relative market preferences of the individual products and the heating value of the products. In calculating the product cost, credits are given for the by-products.

It should be noted that the objective of Phase II of the study is to rank the direct coal liquefaction processes by their relative technical and economic merits and to select the most promising technology for detailed evaluation. Therefore, at this stage of the study, the methodology and accuracy considered for cost estimation and the resulting product costs are adequate primarily for process pre-screening rather than for comparison with the current market prices of existing fuels. More detailed and accurate financial analysis to be used for comparison with fuel cost in the market will be carried out in Phase III of this study.

The preliminary results on technology assessment and process prescreening, incorporating the data on Phase IIB available at the present, are presented in Table 1.

Since the study has not yet been completed, the final conclusions cannot be drawn. However, analysis of the preliminary data presented in the summary table shows that the estimated net yield of naphtha and mid-distillate from Onakawana lignite is in the range of 271 to 482 litres per tonne of moisture-ash-free lignite, depending on the direct liquefaction process selected and ash content in the feed to liquefaction. If LPG is also considered, the estimated total product yields are in the range of 329 to 482 litres per tonne of moisture-ash-free lignite. For non-beneficiated (as-received) lignite, the two-step LSE process seems to be superior to the EDS process even in the bottoms recycle mode of operation.

Comparing the data for processing non-beneficiated (as-received) and beneficiated Onakawana lignite, it is clear that a substantial increase in liquid product yield may be expected in all the integrated beneficiation-liquefaction processes considered. This is particularly true when solid-liquid phase separation techniques (e.g., vacuum distillation, etc.) are employed which is the case for most of the direct liquefaction processes. For the EDS bottoms recycle process, for example, the integrated beneficiation of Onakawana lignite would result in an increase of about 43% in liquid product yields. The liquid product efficiency would increase by about 36%, and the capital investment per annual production of total product would be reduced by about 34%.

In the LSE process, as an exception, filtration is used for separation of solids (unreacted lignite and ash) from lignite-extracted liquid. As previously mentioned, in such a case the amount of liquid product to be used for solids handling will be minimized, thus reducing the effect of high ash content in the feed coal. Therefore, if we assume that trouble-free filtration may be achieved with high ash content in the feed coal, reduction of ash in the feed coal should not substantially increase the product yield and efficiency, although some decrease in capital investment and product cost would result.

Comparing the integrated beneficiation and liquefaction plants based on the LSE, EDS and H-coal processes (the data on RAG/Veba are not available yet) it can be seen that in the plant based on H-coal technology, where a highly active cobalt-molybdenum catalyst is used in ebullated-bed liquefaction reactors, the liquid product yields and the total product yields are as high as about 482 litres per tonne of lignite delivered to the plant (on moisture-ash-free basis). The investment per annual production of hydrocarbons is about 1.6 dollars per litre. The estimated average product price is about 33 cents per litre of liquid product.

The main drawback of this process at the present stage of development is the large amount of Co/Mo catalyst required. Laboratory investigation showed that deactivated Co/Mo catalyst may be regenerated and reused. However, this has not yet been proven on a larger scale. Also, this process has not yet been demonstrated on a pilot-plant scale using lignites.

The EDS process in the bottoms recycle mode of operation seems to be next in rank for an integrated beneficiation and liquefaction plant using Onakawana lignite as a feedstock.

The ranking may be changed after assessment of the four processes is completed. However, it can be seen from the data presented that in some cases the liquid product costs may become comparable with the market prices. This may be even more achievable, if we take into account the possibility of a modular approach for construction of an 8-10,000 tonnes per day plant which would reduce the construction time and the capital investment required. On the other hand, if plant capacity could be increased, due to the predicted addition of about 700 million tonnes of lignite in Ontario, to about 25,000 t/d of beneficiated lignite, the product costs presented in Table 1 would be reduced.

Concerning the quality and upgrading of the liquid products, as the recent data from process developers show, the naphtha could be upgraded to gasoline quality by reforming and hydrotreatment or used as a blendstock with gasoline. The mid-distillate can be upgraded to diesel fuel quality by hydrotreatment and addition of ignition improvers or used, depending on market requirements, as heating oil.

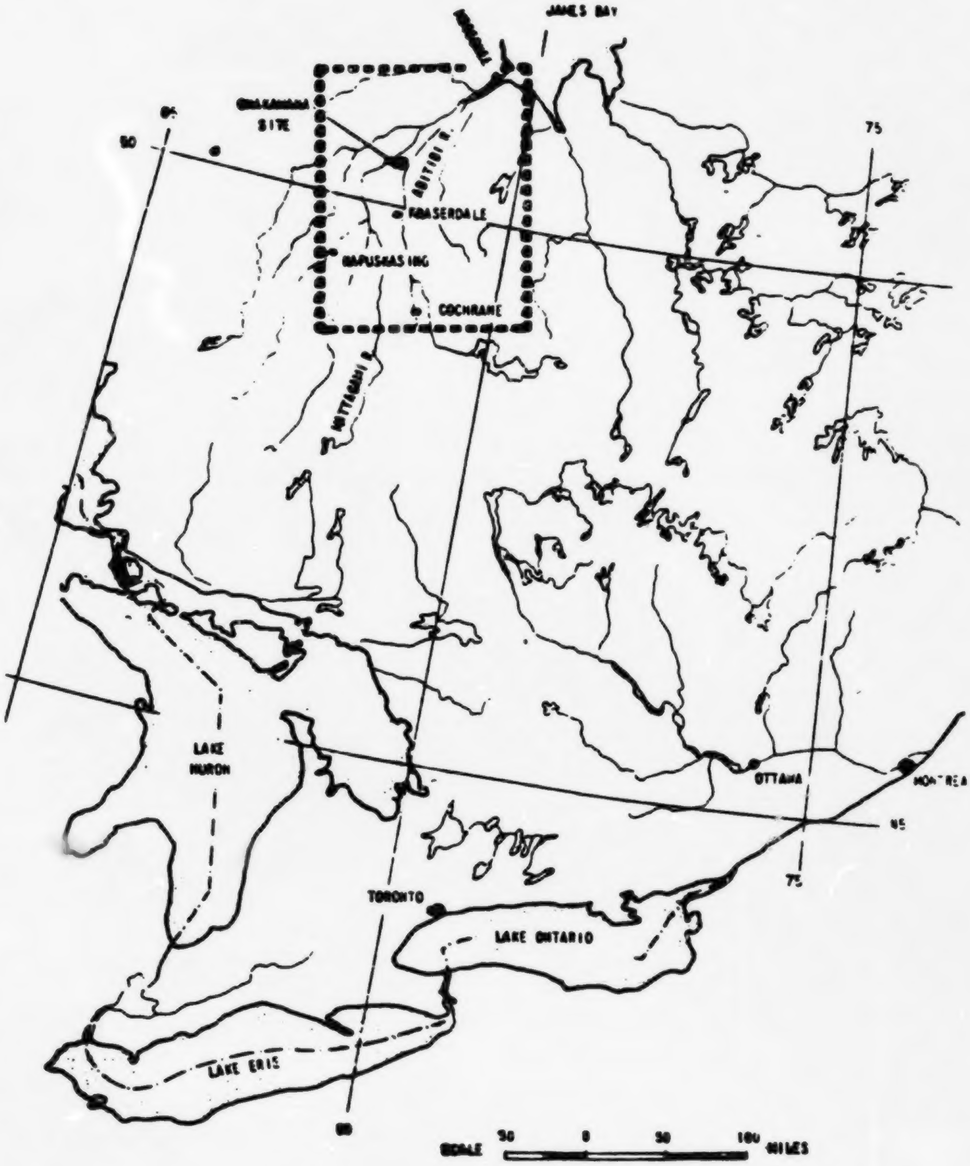
TABLE

Table 1 – Summary of technology assessment
(Feedstock input: 8096 tonnes per day of Onakawana lignite, dry lignite basis, 19.5 wt % ash)

Process	Non-beneficiated (as-received) lignite liquefaction		Integrated beneficiation liquefaction		
	LSE	EDS	LSE	EDS	H-coal
Products m^{3}d					
Propane LPG	165	285	168	272	–
Butane LPG	56	98	56	89	–
Naphtha	919	1532	905	1396	1513
Mid-distillate	1754	231	1834	1121	1626
Product yield, litre/tonne of MAF lignite to plant					
Naphtha and mid-distillate	410.2	270.5	420.3	386.2	481.7
Total product (incl. LPG)	444.1	329.2	454.7	441.5	481.7
Product efficiency, %					
Naphtha and mid-distillate	57.5	37.4	58.9	51.0	63.1
Total product (incl. LPG)	61.2	42.9	62.7	55.8	63.7
Capital investment, $ million	2288.06	1969.38	2226.01	1730.08	1541.61
Investment, $/annual litres of Naphtha and mid-distillate	2.76	3.60	2.62	2.22	1.58
Investment, $/annual litres of total product (incl. LPG)	2.55	2.96	2.42	1.94	1.58
Average product cost $/GJ	11.94	15.21	11.55	10.41	9.25
Individual product cost, /litre					
Propane LPG	44.86	44.83	43.50	32.56	–
Butane LPG	50.17	56.46	48.64	41.01	–
Naphtha	47.96	58.99	46.50	42.85	32.11
Mid-distillate	42.59	50.07	41.29	38.18	33.50
Average product cost, /litre	44.57	56.03	43.15	40.00	32.83

Note: The cost estimates are presented in mid-1983 constant Canadian dollars

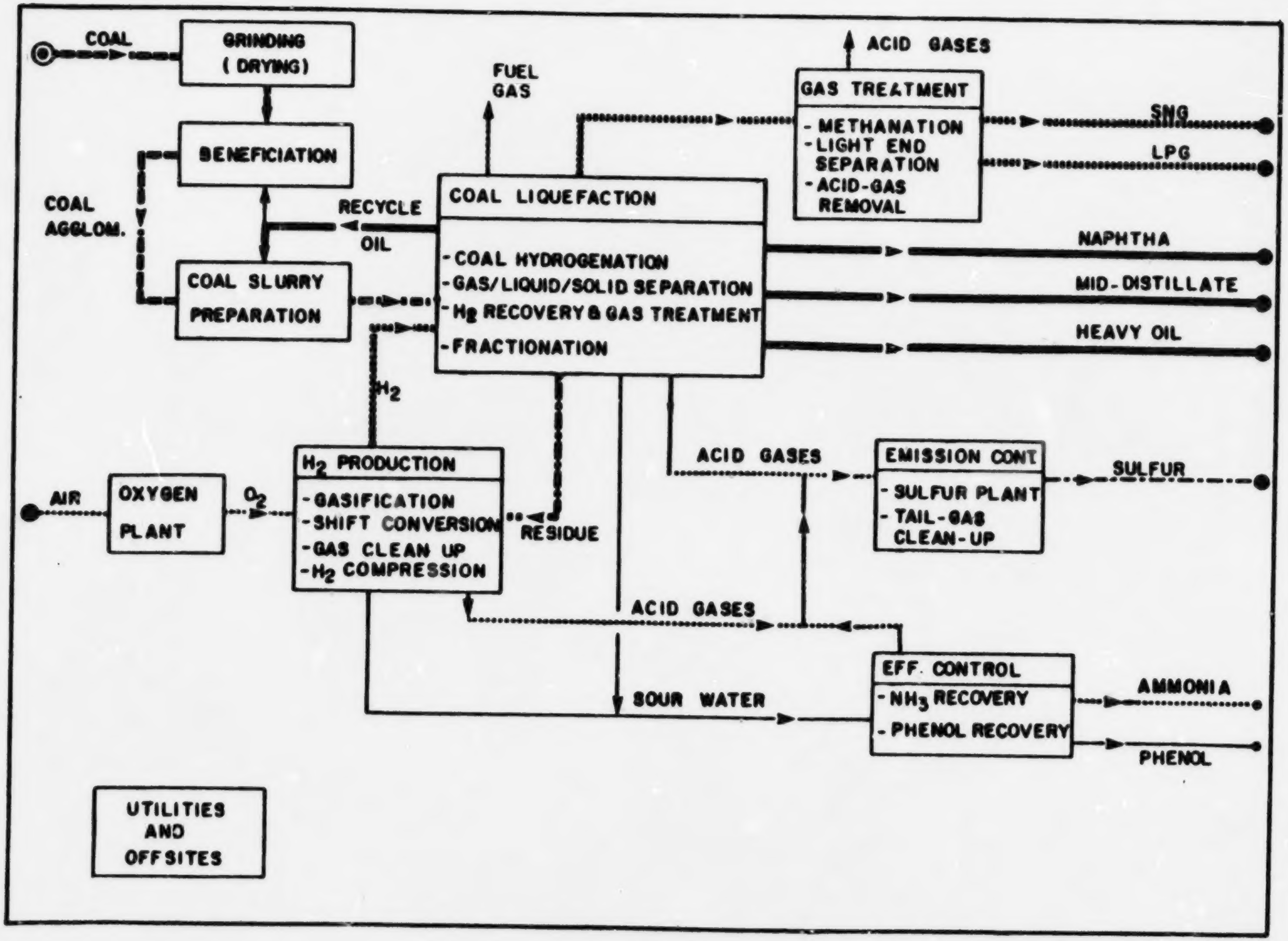
SLIDES


JAMES BAY
MOOSONEE
ONAKAWANA SITE
85
50
ABITIBI R.
FRASERDALE
KAPUSKASING
COCHRANE
MATTAGAMI R.
75
LAKE HURON
OTTAWA
MONTREAL
45
75
TORONTO
LAKE ONTARIO
LAKE ERIE
80
SCALE 50 0 50 100 MILES

Slide 1 – Onakawana lignite deposit

Moisture (run-of-mine), wt %	49.4
Equilibrium moisture, wt %	35.17
Gross calorific value (GVC), MJ/t MF lignite	21,813
Proximate analysis, wt % MF lignite	
Volatile matter	38.9
Fixed carbon	41.6
Ash	19.5
Ultimate analysis, wt % MF lignite	
Carbon	55.0
Hydrogen	3.9
Nitrogen	0.6
Sulphur	1.1
Oxygen	19.9
Ash	19.5
Petrographic analysis, vol %	
Huminites	73.0
Liptinite	2.4
Inertinite	20.4
Mineral matter	4.2

Slide 2 – Typical ultimate, proximate and petrographic analyses of Onakawana lignite


COAL
GRINDING
(DRYING)
BENEFICIATION
COAL AGGLOM.
COAL SLURRY PREPARATION
RECYCLE OIL
FUEL GAS
COAL LIQUEFACTION
- COAL HYDROGENATION
- GAS/LIQUID/SOLID SEPARATION
- H_2 RECOVERY & GAS TREATMENT
- FRACTIONATION
ACID GASES
GAS TREATMENT
- METHANATION
- LIGHT END SEPARATION
- ACID-GAS REMOVAL
SNG
LPG
NAPHTHA
MID-DISTILLATE
HEAVY OIL
H_2
AIR
OXYGEN PLANT
O_2
H_2 PRODUCTION
- GASIFICATION
- SHIFT CONVERSION
- GAS CLEAN UP
- H_2 COMPRESSION
RESIDUE
ACID GASES
EMISSION CONT.
- SULFUR PLANT
- TAIL-GAS CLEAN-UP
SULFUR
ACID GASES
SOUR WATER
EFF. CONTROL
- NH_3 RECOVERY
- PHENOL RECOVERY
AMMONIA
PHENOL
UTILITIES AND OFFSITES

Slide 3 – Typical block diagram of an integrated plant

Lignite feed:	8096 t/d to the plant (dry lignite basis)
Constant Canadian dollars:	Mid-1983
Plant location:	Within 4.5 km (3 miles) of the lignite mine
Construction period:	4 years
Capital investment schedule:	(S-type curve)
Plant life:	30 years
Depreciation:	Straight-line method
Salvage value:	Zero
Process contingency:	5%
Project and estimating contingency:	10%
Plant service factor:	0.85 (310 operating days per year)
Working capital:	3% of installed-plant cost
Capital financing:	Debt/equity 70/30%
Debt cost:	5% per annum (constant dollars)
Return on equity:	10% per annum (before taxes)
Lignite cost:	$15 per tonne at equilibrium moisture
Electricity cost:	3.0 cents/KWH
By-product credits:	
Sulphur	$ 65/t
Ammonia	$300/t
Mixed phenols	$250/t

Slide 4 – Financial assumptions and economic criteria

SESSION I: PAPER 5

THERMAL AND CATALYTIC LIQUEFACTION OF NOVA SCOTIA COALS

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Nova Scotia Research Foundation Corporation
Dartmouth, Nova Scotia

ABSTRACT

Process studies on high-pressure donor solvent extraction and catalytic hydrogenation of Sydney area coals are described. Lingan, Prince and No. 26 high-volatile bituminous coals were liquefied in a 2 kg/hour continuous-flow pilot unit. Results of a statistical investigation to evaluate the effects of coal feedstock, reaction temperature and slurry space velocity on product composition are presented. Hub seam coal from the Prince mine was found to be the most reactive feedstock at thermal liquefaction conditions. Within the Harbour seam reactivity was observed to decrease going from the Lingan mine to No. 26. Simple correlations were drawn between individual coal properties, both chemical and petrographic, and product yields. Conversions and product distributions are reported for catalytic hydrogenation using commercially available Ni/Mo and Co/Mo hydrotreating catalysts. A recently initiated test program on a thermal/catalytic two-stage process configuration designed to improve hydrogen utilization, increase distillate yield and reduce the production of hydrocarbon gases is also discussed.

**denotes speaker*

PRÉSENTATION 5

LA LIQUÉFACTION THERMIQUE ET CATALYTIQUE DES CHARBONS DE LA NOUVELLE-ÉCOSSE

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Fondation de recherche de la Nouvelle-Écosse
Dartmouth (Nouvelle-Écosse)

RÉSUMÉ

Cette communication décrit les études sur les procédés d'extraction par solvant donneur à haute pression et les procédés d'hydrogénation catalytique des charbons de la région de Sydney. Des charbons bitumineux très volatils Lingan, Prince et nº 26 ont été liquéfiés dans une installation pilote en continu de 2 kg/heure. Elle présente les résultats d'une étude statistique permettant d'évaluer les effets de la charge d'alimentation en charbon, de la température de réaction et de la vélocité de l'espace semi-liquide sur la composition du produit. On a constaté que le charbon du gîte central de la mine Prince s'avérait la charge d'alimentation qui réagissait le plus aux conditions de liquéfaction thermique. Pour le gîte Harbour, on a constaté que la réactivité diminuait au fur et à mesure qu'on s'éloignait de la mine Lingan, vers la mine nº 26. On a établi des corrélations simples entre les caractéristiques spécifiques du charbon, tant chimiques que pétrographiques, et les rendements de produits. Les conversions et les répartitions de produits sont présentées dans le cas de l'hydrogénation catalytique, en utilisant des catalyseurs d'hydrotraitement Ni/Mo et Co/Mo disponibles sur le marché. Un programme d'essais récent, retenant un procédé thermique/catalytique en deux étapes, conçu pour améliorer l'utilisation de l'hydrogène, et qui accroît la production de distillat tout en réduisant la production de gaz d'hydrocarbures est également présenté.

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THERMAL AND CATALYTIC LIQUEFACTION OF NOVA SCOTIA COALS

INTRODUCTION

The production of liquid fuels from coal was practiced on an industrial scale in Germany during the second world war. In the decade following World War II a direct coal liquefaction plant was built in the United States and a synthetic fuels industry based on coal was established in South Africa. Development work on coal liquefaction in North America diminished after a few years due to the low price and ready availability of crude oil. However, since the early 1970s the United States and several other industrialized nations around the world have focused considerable attention on the production of liquid fuels from coal.

The increased activity was stimulated by an upward trend in crude oil prices and a delicate supply/demand balance for petroleum products. In the early 1980s a number of large pilot plants were operated in the United States to determine the technical and economic feasibility of direct coal liquefaction. Within the last two years, however, crude oil prices have stabilized and declined slightly. This has resulted in the cancellation or slowdown of most large-scale synfuels projects in North America. Nevertheless, in other parts of the world industrialized countries, including Germany and Japan, are actively pursuing and demonstrating advances in coal liquefaction technology.

Although Canada has abundant coal reserves, the Canadian Government has not made a commitment to developing a coal liquefaction process because of the enormous costs involved. On the other hand, the Canadian way of life is highly dependent on petroleum liquids. Since our existing crude supplies are not expected to meet our future liquid fuel demands, it seems that we will have to rely on synthetic liquid fuels to some degree in the next few decades. Furthermore, since long lead times are involved in process evaluation, detailed design and plant construction, it is essential to understand the basic concepts of the promising liquefaction processes and verify their projected yield structures as they apply to Canadian coals.

Process studies relating to the direct liquefaction of Nova Scotia high-volatile bituminous coals were initiated at NSRFC in the latter part of 1977. Since that time five phases of work have been completed. Extensive experimental studies have been carried out on a low-severity extractive coking process (1,2,3), medium-to high-pressure donor solvent extraction (4,5) and single-stage catalytic hydrogenation (6). At present, efforts are being concentrated on a two-stage thermal/catalytic process configuration. Since 1977 R&D activities at NSRFC have progressed from batch autoclave work to the design, assembly and operation of continuous processing units for both coal liquefaction and the catalytic upgrading of coal-derived liquids.

DONOR SOLVENT LIQUEFACTION

Historically, two routes have been used to produce liquid fuels from coal – a direct or degradation route and an indirect or synthesis route. High-volatile bituminous coals, similar to those of the Sydney coalfield, are considered to be very good feedstocks for direct liquefaction. Proximate and ultimate analysis of coals tested are presented in Table 1. Petrographic analyses are given in Table 2.

Direct liquefaction via solvent extraction involves contacting coal at temperatures up to 500°C with a coal-derived liquid containing hydrogen donor compounds. Molecular hydrogen may be supplied under pressure during the extraction stage, and used to hydrogenate the recycle liquid or both. After the solvation step, techniques such as filtration, centrifugation, coking, etc., are used to separate the coal liquids from the unreacted coal, ash and char. Much of the work on direct liquefaction today is based on concepts originated in Germany more than 50 years ago. The Pott-Broche process was the earliest development based on solvent extraction (7, 8).

Role of Donor Solvent

The solvent plays an important role in this process, serving as a transport medium, a coal solvent and a vehicle to transfer hydrogen to the coal. Within the past few decades several investigators (9-13) have reported on the mechanism by which hydrogen is transferred from a hydrogen donor solvent to coal during the liquefaction process. It is widely accepted that coal is dissociated by thermal decomposition into free-radicals which achieve stabilization by the capture of hydrogen atoms from donor molecules. Experimental work has proven hydroaromatic compounds to be effective hydrogen donors under liquefaction conditions.

Preparation of Donor Solvent

Anthracene oil was used as the starter feedstock to prepare hydrogen donor solvent. A highly aromatic coal-derived oil, it was expected to perform adequately in coal extraction after its hydrogen content was adjusted in the range of

8-9%. The characteristics of the raw oil are shown in Table 3. Solvents with varying hydrogen content have been prepared from anthracene oil using a fixed-bed catalytic hydrotreater. The bench-scale unit is described elsewhere (3).

A commercial Co/Mo/Al hydrotreating catalyst, Nalcomo 479, was used to prepare solvents containing 7.5 and 9% hydrogen. These oils were used for the catalytic and thermal liquefaction experiments described herein. The characteristics of the hydrogenated oils are given in Table 3. Proton distribution illustrates that the 9% H oil, HAO 56, contains a high level of transferrable hydrogen, H_β. The chemical and physical properties of Nalcomo 479 catalyst are presented in Table 4. The operating conditions used to produce these solvents are reported elsewhere (6).

Effects of Process Variables on Donor Solvent Extraction Yields

In order to evaluate the effects of coal feedstock, reaction temperature, total pressure and slurry feedrate on product composition, a series of sixteen experiments were conducted according to a 2^4 factorial design. The donor solvent experiments were conducted in a continuous-flow unit with Prince Hub seam and Lingan Harbour seam coals. The bench-scale unit has been described previously (5) and is shown in Figure 9. The runs were made in a once-through mode using 9% H oil as donor vehicle. The concentration of coal in the feed slurry was fixed at 30 wt %. Hydrogen treatrate was ca 7.5 wt % based on dry coal. The operating conditions investigated were as follows:

Reactor temperature, °C	440, 460
Back pressure, MPa	17.24, 20.68
Slurry feedrate, kg/hr	1, 2.

In this study the slurry hourly space velocity is 1.0 at a slurry feedrate of 1 kg/hr. A typical run was of 6-8 hours' duration. During the steady-state operating period vent gas streams were sampled and other product streams were collected for analytical and material balance purposes.

In these experiments the following definitions for the product fractions isolated by solvent extraction were used:

- Oil – pentane solubles
- Asphaltenes – benzene solubles, pentane insolubles
- Preasphaltenes – THF solubles, benzene insolubles.

A direct extraction technique was used to determine these fractions. Individual samples of product slurry were separately extracted with pentane, benzene, and tetrahydrofuran (THF). Conversions were calculated on the basis of maf coal fed to the reactor during the steady-state sampling period and unconverted coal in the dry insoluble residues.

Table 5 summarizes the results of the coal hydrogenation parameter study. An examination of the data indicates that the controlled variables studied certainly do affect product distribution. A statistical evaluation of the data was carried out to determine the significance of the observed effects. The response variables selected for the statistical analysis included gas make, oil yield, asphaltenes, preasphaltenes and hydrogen consumption. A standard analysis of variance was used to establish confidence levels.

Temperature was found to have a significant effect on the conversion of coal to the products listed. Increasing the operating temperature from 440 to 460°C produced higher yields of gases and oil and lower yields of asphaltenes and preasphaltenes. For example, a comparison of run no. 3116 at 440°C and run no. 3111 at 460°C shows the following shift in product distribution:

- gases increased from 9.3 to 13.3%
- oil increased from 24.7 to 30.8%
- asphaltenes decreased from 29.8 to 25.1%
- preasphaltenes decreased from 20.5 to 16.1%.

The effect of pressure was only significant with regard to gas make and hydrogen consumption. Increasing the operating pressure from 17.24 to 20.68 MPa had a negative effect on gas make and a positive effect on hydrogen consumption. For example, in run no. 3117 at 17.24 MPa the gas make was 20.4% compared with 17.7% in run no. 3115 at 20.68 MPa. Furthermore, the hydrogen consumption in run no. 3117 was 1.7% compared with 2.0% in run no. 3115.

Slurry feedrate was found to significantly affect the yields of gases, oil and preasphaltenes. Increasing the slurry feedrate produced lower yields of gases and oil and higher yields of preasphaltenes. A comparison of run no. 3112 at 1 kg/hr and run no. 3116 at 2 kg/hr shows the following shift in product distribution:

- gases decrease from 12.1 to 9.3%
- oil decreases from 31.0 to 24.7%
- preasphaltenes increase from 15.6 to 20.5%.

The statistical evaluation shows that coal feedstock significantly affects product distribution and hydrogen consumption. Continuous runs with the Prince coal produced higher gas makes, higher oil yields and lower yields of preasphaltenes than runs with the Lingan coal at similar operating conditions. In general, hydrogen consumption was higher with the Prince mine coal. The following comparison illustrates the effect of coal feedstock on yields and hydrogen consumption:

	Run no. 3115 Prince batch D	Run no. 3125 Lingan batch K
Products, wt %		
Gases	17.7	14.8
Oil	33.0	26.2
Asphaltenes	25.8	26.7
Preasphaltenes	11.9	19.4
Hydrogen consumption, wt %	2.0	1.4

Dependence of Product Distribution on Coal Properties

In addition to the feedstocks used in the coal hydrogenation parameter study, four other coals were tested (Prince batch C, Lingan batch I, Lingan batch J and No. 26 batch B). Continuous experiments were carried out at operating conditions judged best to maximize oil yield. Results are presented in Table 6. The product distributions show that oil yield varied from 21.0 to 29.6% and product preasphaltenes ranged from 13.4 to 23.7%. Conversions for the Lingan coals were quite similar. Run no. 3135 made with No. 26 colliery coal produced the lowest oil yield, 21.0%, and the highest yield of preasphaltenes, 23.7%.

It is well recognized that the liquefaction behaviour of a coal is dependent on both its chemical and petrographic characteristics (14,15). Figures 1-7 are presented to illustrate the variation of conversion with individual coal properties.

Figures 1 and 2 indicate that pyritic and organic sulphur both have a positive influence on coal conversion. At higher concentrations of these constituents, oil yield is enhanced and there is a substantial decrease in the preasphaltenes fraction. A similar trend is apparent for ash content as shown in Figure 4.

The influence of carbon on conversion is presented in Figure 5. The highest conversions to benzene solubles plus gases were found for coals with 73-78% carbon. Plotting conversion against vitrinite content, Figure 6, gave scattered points for coals containing 74-81 volume % vitrinite. Since five of the six points were in that region no correlation was drawn. The effect of coal rank on conversion is shown in Figure 7. Coal rank is presented in terms of maximum reflectance of vitrinite (% R_o max.). Figure 7 shows that the degree of conversion to benzene solubles plus gases increases significantly as rank decreases. The highest oil yield, 33%, was produced from Prince coal, 0.78% R_o max.

Although Figures 1-7 suggest that simple correlations exist between coal conversion and individual coal properties, it must be kept in mind that conversion is influenced by several properties interacting simultaneously.

CATALYTIC HYDROGENATION

Catalytic hydrogenation adds hydrogen to coal with the aid of a suitable catalyst. Bergius (16) conducted experimental work on catalytic hydrogenation of brown coals from 1913-1924 and the first commercial plant was built in 1927. However, during the past 10-15 years significant advances have been made relating to the catalytic hydrogenation of coal. H-coal (17), one of the more advanced processes developed in the United States, utilizes a catalyst in particulate form to hydrogenate a coal-oil slurry in an ebullated bed. In West Germany a direct liquefaction process is being developed by Ruhrkohle AG and Veba Oel AG that utilizes an inexpensive disposable catalyst (18).

Process Variable Study on Lingan Harbour Seam Coal

A series of experiments were carried out on Lingan Harbour coal at medium-severity operating conditions to investigate conversion and product yields. In this study pulverized catalyst was added to the feed slurry to simulate single-stage catalytic coal liquefaction. The experiments were conducted varying reaction temperature, slurry space velocity, hydrogen treatrate, vehicle oil composition, catalyst type and catalyst concentration. Lingan batch L coal was used. Runs were of 6-8 hours' duration. A summary of operating conditions and performance is shown in Table 7.

The first three experiments, run no. 5005-5007, were carried out at 460°C and 17.24 MPa. The concentration of coal in the feed slurry was fixed at 29.5 wt %. A commercially available Ni/Mo hydrotreating catalyst, Nalco NM 502, was used. In run no. 5005 the slurry feedrate was 1 kg/hr. Catalyst concentration was fixed at 4 wt % based on maf coal and hydrogen treatrate was 7.5 wt % based on dry coal. The coal conversion and oil yield produced were 91.0 and 29.9%, respectively. In run no. 5006 catalyst concentration was doubled to 8 wt %. Coal conversion to THF solubles plus gases was similar to that of run no. 5005; however, oil yield increased to 33.1%. In run no. 5007 catalyst was held at the 8 wt % level, hydrogen treatrate was doubled to 15 wt % and slurry feedrate was reduced to 0.8 kg/hr. The changes in hydrogen treatrate and slurry feedrate affected a significant shift in product distribution. Oil yield increased further to 38.2% while preasphaltenes decreased to 7.0%. The gas make in run no. 5007 was 21.9% compared with 17.1% in run no. 5006.

On completion of these baseline runs an optimization study was undertaken. Five experiments were carried out according to a Simplex Self-Directing Evolutionary Operation (SSEVOP). The primary goal of SSEVOP is to locate the optimum operating conditions as quickly as possible when several variables are being considered. In this case temperature, catalyst level, hydrogen treatrate and slurry feedrate were the process variables of interest. The principal response was oil yield.

An analysis of operating data was made to determine the average level and range for each factor. It was judged that a shift of one standard deviation from the mean level in each direction would be acceptable for each factor. The original Simplex design was prepared based on the results of this preliminary analysis. The run conditions established were as follows:

Run no.	Hydrogen treatrate (wt % dry coal)	Catalyst level (wt % maf coal)	Temperature °C	Slurry feedrate (kg/hr)
5009	11	7	451	0.920
5010	15	7	451	0.920
5011	13	10	451	0.920
5012	13	8	467	0.920
5014	13	8	455	1.320

Test results are presented in Table 7. Oil yield ranged from 33.1 to 36.5%. The results of these five runs were used to calculate a new design point.

The operating conditions at the new design point were 455°C, 8% catalyst, 13% hydrogen treatrate and 0.5 kg/hr slurry feedrate. These conditions were similar to those used in run no. 5014 with the exception of slurry feedrate. The new design point could not be run, however, because previous attempts to operate the metering pump at this level were unsuccessful. In consideration of these facts run no. 5015 was conducted at a slurry feedrate of 0.9 kg/hr, the midpoint between the new design point and the feedrate used in run no. 5014. A comparison of results from run no. 5014 and 5015 shows that the decrease in slurry feedrate from 1.3 to 0.9 kg/hr did not affect oil yield substantially.

Two experiments were carried out to investigate catalyst type and vehicle oil composition. American Cyanamid HDS-1442, a Co/Mo hydrotreating catalyst, was used in run no. 5016. A comparison of run no. 5007 and 5016 shows a higher oil yield with the Ni/Mo catalyst. These results are in agreement with our earlier findings using a batch autoclave system for catalyst screening tests.

Hydrogenated anthracene oil containing 7.5 wt % hydrogen was used as vehicle oil in run no. 5005-5016 inclusive. In run no. 5017 hydrogenated anthracene oil with a hydrogen content of 9% was used. A comparison of product yields from run no. 5015 and 5017 shows that a small improvement in oil yield was achieved using 9% H vehicle oil. The highest coal conversion and oil yield achieved at medium-severity operating conditions were 92 and 38%, respectively.

Comparison of Lingan Harbour, Prince Hub and Illinois No. 6 Coal Reactivity

In this section duplicate runs conducted with Prince Hub and Illinois No. 6 (Burning Star Mine) are compared with a single run on Lingan Harbour coal. The operating conditions were as follows: 451°C, 17.24 MPa, 13% hydrogen treatrate and 0.92 kg/hr slurry feedrate. Nalco NM 502 catalyst was used at a 10 wt % level. Test results are presented in Table 8.

An examination of the data shows that high levels of conversion to THF solubles plus gases were achieved with all three coal feedstocks. In fact, total coal conversion ranged from 90.5 to 93.6%. However, product distributions were significantly different. For example, run no. 5011 with Lingan coal produced 36.1% oil whereas the oil yields for Prince and Illinois No. 6 averaged 41.8 and 57.3%, respectively. Furthermore, the results show that in the case of the Nova Scotia coals the conversion products contain high levels of asphaltenes and preasphaltenes. The asphaltene-preasphaltene components in Lingan raw product totalled 38.7%. This is more than double the 16% yield of these components measured in Illinois No. 6 raw product.

The three coals differ in their chemical and petrographic characteristics as shown in Tables 1 and 2. With regard to chemical characteristics Lingan has lower ash and sulphur levels than Illinois No. 6. Prince Hub, on the other hand, has high ash and sulphur levels similar to those of Illinois No. 6. However, on the basis of results presented here and our previous experimental work, the difference in reactivity is primarily attributable to rank. Product yields are plotted as a function of coal rank in Figure 8. Coal rank is presented in terms of maximum reflectance of vitrinite (% R_o max.). Figure 8 shows that oil yield increases as coal rank decreases. The highest oil yield, 57%, was produced from Illinois No. 6 coal, R_o max. 0.62%. In conclusion, the order of reactivity was found to be: Illinois No. 6 > Prince Hub > Lingan Harbour.

Improved Performance on Lingan Coal at Increased Severity

Additional experiments were conducted with Lingan coal at increased severity in an attempt to achieve higher oil yields. The operating conditions and test results for the higher severity operations are given in Table 9.

Severity was increased step-wise in advancing from run no. 5021 to 5024. In run no. 5021 the level of Nalco NM 502 catalyst was increased to 20 wt %; other operating conditions were similar to those of run no. 5011. The effect of the higher catalyst concentration on product distribution was small. Temperature was increased to 460°C in run no. 5022 and slurry feedrate was reduced to 0.7 kg/hr in run no. 5023. The changes in temperature and slurry feedrate resulted in a gradual but persistent shift towards lighter products. In run no. 5024 pressure was increased to 20.68 MPa and 9% H vehicle oil was used. This run produced the highest oil yield, 47.1% and the lowest yield of asphaltene-preasphaltene components, 18.5%. Run no. 5026 was carried out at 460°C, 20.68 MPa and 10 wt % catalyst. The reduction in catalyst concentration had a significant negative effect on product distribution.

These catalytic hydrogenation runs suggest that oil yields in the range of 50% can be produced from Lingan Harbour and Prince Hub coals in a single-stage catalytic process. Furthermore, the tests suggest that in order to achieve oil yields in this range the Nova Scotia coals would require higher catalyst consumption rates than Illinois No. 6. In fact, it appears that catalyst requirements would be 2-3 times higher for the Nova Scotia coals.

TWO-STAGE THERMAL/CATALYTIC LIQUEFACTION

In recent years advances have been made to improve so-called conventional coal hydrogenation. The new process developments are centered on liquefying coal in two separate reaction zones. Chevron Research has used two separate but closely coupled reaction zones to achieve high liquid yields and control hydrogen consumption (19). C-E Lummus has reported on an integrated two-stage liquefaction process which combines short contact time thermal liquefaction of coal and LC-Fining hydrotreatment of the extract after it has been deashed (20). Additionally, Hydrocarbon Research Inc. is currently investigating two-stage catalytic/catalytic liquefaction (21) and Kerr-McGee is developing a two-stage option utilizing their critical solvent deashing process (22).

In July 1984, NSRFC initiated studies on two-stage thermal/catalytic liquefaction. In the process coal is solubilized in the thermal first stage and subsequently upgraded in the catalytic second stage. By using two separate reaction zones the thermal dissolution and the catalytic upgrading steps can be independently optimized to maximize efficiency and control product distribution and quality. It is expected that the process will improve hydrogen utilization, increase distillate yield and reduce the production of hydrocarbon gases. Testwork has been conducted on both stages separately using our existing coal liquefaction unit.

First-Stage Dissolution Studies

A series of eight experiments were conducted according to a factorial design to investigate the effects of temperature, pressure and coal space velocity on conversion in the thermal stage. Lingan batch L coal was used in these experiments. Hydrogenated anthracene oil containing 9.0% H was used as the donor vehicle. The concentration of coal in the feed slurry was fixed at 30 wt %. Hydrogen treatrate was ca. 7.5 wt % based on dry coal. The operating conditions investigated were as follows:

Temperature, °C	440, 460
Back pressure, MPa	6.89, 10.34
Slurry feedrate, kg/hr	1, 2.

The objective in the thermal stage is to affect high coal conversion and low hydrocarbon gas production. Results presented in Table 10 show that operating conditions can be selected to achieve the desired objective. A statistical evaluation of the data was carried out to determine the significance of the observed effects. The response variables selected for the statistical analysis included gas make, oil yield, asphaltenes and preasphaltenes. A standard analysis of variance was used to establish confidence levels.

Temperature was found to be highly significant with respect to the production of gases and preasphaltenes. Increasing the temperature from 440 to 460°C produced higher gas yields and lower yields of preasphaltenes. For example, a comparison of run no. 5031 at 440°C and run no. 5029 at 460°C shows the following shift in product distribution:

- gases increased from 12.5 to 20.9%
- preasphaltenes decreased from 24.1 to 18.3%.

The statistical evaluation shows that the effect of pressure, over the range 6.89 to 10.34 MPa, is not highly significant with regard to any of the response variables evaluated.

Slurry feedrate was found to significantly affect the yields of gases, asphaltenes and preasphaltenes. Increasing the slurry feedrate produced lower yields of gases and asphaltenes and higher levels of preasphaltenes. For example, a comparison of run no. 5031 at 1 kg/hr and run no. 5033 at 2 kg/hr shows the following shift in product distribution:

- gases decreased from 12.5 to 8.9%
- asphaltenes decreased from 27.3 to 25.2%
- preasphaltenes increased from 24.1 to 31.2%.

Non-Integrated Two-Stage Liquefaction Trials

A very limited number of non-integrated two-stage liquefaction trials have been conducted. In these experiments thermal stage product was collected over a 10-13 hr operating period and subsequently upgraded. The thermal dissolution step and the catalytic upgrading step were separated by approximately 48 hours. The catalytic stage was operated at temperatures of 390 and 430°C, 17.24 MPa and slurry feedrates of 1.15 and 0.75 kg/hr. The highest oil yield achieved was 37% using 20 wt % Ni/Mo catalyst. Test results suggest, however, that higher oil yields can be achieved with minimum gas production by reducing slurry space velocity in the catalytic stage.

It should be noted at this point that first-stage products may undergo regressive (condensation) reactions upon storage and/or thermal cycling between stages. This can render the initial products unresponsive to subsequent catalytic conversion and increase the production of light gas. Hence, a catalytic reactor is presently being added to the existing unit. The two reactors will be closely coupled to permit integrated two-stage operations. The catalytic reactor will be used to contain and control hydrocracking and hydrogenation reactions.

Future work includes further scoping of first- and second-stage operating conditions to optimize selectivity towards distillate products, to be followed by continuous experiments with solvent recycle.

ACKNOWLEDGEMENTS

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TABLES

Table 1 – Analysis of coals tested

Coal description:	Lingan batch I	Lingan batch J	Lingan batch K	Lingan batch L
Moisture, wt %	1.39	1.47	1.23	1.28
Proximate (dry basis) wt %				
Ash	2.82	6.37	3.89	4.10
Volatile matter	38.14	37.02	37.36	34.83
Ultimate (dry basis) wt %				
Carbon	81.40	78.84	81.47	81.78
Hydrogen	5.34	5.00	5.06	5.37
Nitrogen	1.63	1.62	1.70	1.56
Sulphur	1.00	2.69	1.80	1.67
Ash	2.83	6.37	3.89	4.10
Oxygen (by difference)	7.80	5.48	6.08	5.85
Sulphur forms (dry basis) wt %				
Sulphate	0.06	0.07	0.03	0.05
Pyritic	0.54	1.87	1.21	1.05
Organic (by difference)	0.40	0.75	0.56	0.57
Total	1.00	2.69	1.80	1.67
Free swelling index	8	8	8	8

Coal description:	Prince batch C	Prince batch D	Prince batch B	Illinois No. 6
Moisture, wt %	2.43	1.98	0.88	3.17
Proximate (dry basis) wt %				
Ash	6.42	9.23	4.00	11.13
Volatile matter	36.54	36.22	34.60	38.05
Ultimate (dry basis) wt %				
Carbon	77.23	73.48	80.30	68.73
Hydrogen	4.86	4.80	5.20	4.73
Nitrogen	1.55	1.45	1.67	1.39
Sulphur	3.04	4.22	1.11	3.46
Ash	6.42	9.23	4.00	11.13
Oxygen (by difference)	6.90	6.82	7.72	10.56
Sulphur forms (dry basis) wt %				
Sulphate	0.28	0.18	0.05	0.01
Pyritic	1.39	2.25	0.42	1.50
Organic (by difference)	1.37	1.79	0.64	1.95
Total	3.04	4.22	1.11	3.46
Free swelling index	2 ½	2	8	1 ½

Table 2 – Petrographic characteristics of coal tested

Coal description:	Lingan batch I	Lingan batch J	Lingan batch K	Lingan batch L
Maceral composition (% by volume)				
Vitrinite	75.6	81.2	74.6	77.0
Exinite	6.2	5.3	7.4	4.2
Inertinite	18.0	9.9	17.4	16.4
Macrinite	(2.8)	(1.5)	(1.6)	(2.6)
Micrinite	(6.2)	(1.7)	(4.4)	(4.4)
Semifusinite	(5.8)	(1.9)	(6.6)	(4.6)
Fusinite	(3.2)	(4.8)	(4.8)	(4.8)
Mineral matter	0.2	3.6	0.6	2.4
Pyrite	(0.2)	(3.2)	(0.4)	(0.6)
Quartz	–	–	–	(0.4)
Shale	–	(0.2)	–	(1.4)
Calcite	–	(0.2)	(0.2)	–
% R_o Max.	0.94	0.92	0.98	0.96

Coal description:	Prince batch C	Prince batch D	Prince batch B	Illinois No. 6
Maceral composition (% by volume)				
Vitrinite	76.8	74.7	85.2	79.2
Exinite	3.1	4.1	3.2	3.8
Inertinite	18.5	18.0	11.2	11.8
Macrinite	(1.4)	(0.8)	(1.8)	(0.6)
Micrinite	(5.9)	(5.4)	(3.6)	(4.6)
Semifusinite	(4.1)	(5.4)	(3.6)	(2.8)
Fusinite	(7.1)	(6.4)	(2.6)	(3.8)
Mineral matter	1.6	3.2	0.4	5.2
Pyrite	(1.0)	(2.6)	(0.2)	(1.4)
Quartz	–	–	(0.2)	(1.4)
Shale	(0.4)	(0.4)	–	(2.4)
Calcite	(0.2)	(0.2)	–	–
% R_o Max.	0.83	0.78	1.08	0.62

Table 3 – Characteristics of raw and hydrogenated anthracene oil

Sample description	Raw anthracene	HAO 55	HAO 56
Specific gravity, 60/60°F	1.135	1.073	1.033
Carbon, wt %	91.03	91.58	90.36
Hydrogen, wt %	5.65	7.54	9.01
Nitrogen, wt %	0.97	0.41	0.13
Sulphur, wt %	0.62	0.062	0.006
Oxygen, wt %	1.29	0.96	1.06
Proton distribution, %			
H_{ar} (9-6 ppm)	86.21	36.49	16.34
Hα (3.5-2 ppm)	11.30	31.75	33.26
Hβ(2-1.1 ppm)	1.48	24.57	37.77
Hγ (1.1-0.4 ppm)	1.01	7.18	12.63
Distillation data, °C (ASTM D-1160)			
IBP	227	188	177
10%	270	251	251
20%	301	282	277
30%	320	300	294
40%	336	312	305
50%	348	323	314
60%	362	334	323
70%	375	347	336
80%	390	366	356
90%	416	387	384
95%	455	404	405
EP	470	438	437

Table 4 – Chemical and physical properties of hydrotreating catalysts

	Nalco NM 502	HDS-1442	Nalcomo 479
MoO_3, wt %	14.0	13.2	19.0
NiO, wt %	4.0		
CoO, wt %		3.5	4.4
Size, cm	0.16	0.16	0.16
Surface area, M²/g	240	300	180
Pore volume, cc/g	0.53	0.80	0.47
Density, g/cc	0.73-0.74	0.58	0.82-0.84
Crush strength, kg	6.4 -7.3	6.2	6.4 -7.3

Nalco NM 502 and Nalcomo 479 are manufactured by the Nalco Chemical Company

HDS-1442 is manufactured by American Cyanamid

Table 5 – Summary of results from coal hydrogenation parameter study using continuous-flow unit

Run no.	3110	3112	3114	3116	3115	3117	3118	3111
Temperature, °C	440	440	440	440	460	460	460	460
Back pressure, MPa	20.68	17.24	20.68	17.24	20.68	17.24	20.68	17.24
Slurry feedrate, kg/hr	1.034	0.995	1.968	2.039	1.017	0.982	2.020	2.060
H_2 consumption, wt % maf coal	1.6	1.3	1.6	1.1	2.0	1.7	1.6	1.3
Conversions, wt % of maf coal								
Pentane solubles plus gases	43.9	43.1	35.8	34.0	50.7	50.1	45.2	44.1
Benzene solubles plus gases	71.1	71.3	64.4	63.8	76.5	75.7	70.4	69.2
THF solubles plus gases	87.1	86.9	84.9	84.3	88.4	87.9	86.9	85.3
Product distribution, wt % of maf coal								
C_1-C_2	3.8	4.6	2.9	3.1	7.3	8.0	5.1	5.5
C_3	1.8	1.8	1.2	1.7	3.8	3.6	2.6	2.2
C_4	1.6	2.3	1.6	1.5	2.6	3.4	2.0	2.1
NH_3, H_2O, H_2S, CO_x	2.6	3.4	2.8	3.0	4.0	5.4	3.2	3.5
Oil	34.1	31.0	27.3	24.7	33.0	29.7	32.3	30.8
Asphaltenes	27.2	28.2	28.6	29.8	25.8	25.6	25.2	25.1
Preasphaltenes	16.0	15.6	20.5	20.5	11.9	12.2	16.5	16.1
Run no.	3129	3127	3126	3124	3125	3123	3122	3128
Temperature, °C	440	440	440	440	460	460	460	460
Back pressure, MPa	20.68	17.24	20.68	17.24	20.68	17.24	20.68	17.24
Slurry feedrate, kg/hr	0.999	1.042	2.020	1.984	1.038	1.087	1.996	2.045
H_2 consumption, wt % maf coal	1.4	1.0	1.4	1.0	1.4	1.3	1.4	1.4
Conversions, wt % of maf coal								
Pentane solubles plus gases	30.0	33.0	24.2	24.8	41.0	42.2	35.0	35.5
Benzene solubles plus gases	59.9	60.7	52.0	52.9	67.7	68.4	61.6	60.8
THF solubles plus gases	85.7	85.8	83.2	81.9	87.1	86.5	84.9	85.5
Product distribution, wt % of maf coal								
C_1-C_2	4.0	3.9	2.5	2.9	7.0	7.6	4.8	5.0
C_3	1.5	1.4	0.9	1.0	3.0	3.5	2.4	2.2
C_4	1.8	1.9	1.3	1.5	2.4	2.8	2.2	2.1
NH_3, H_2O, H_2S, CO_x	2.1	2.1	2.1	1.8	2.4	2.1	1.9	2.9
Oil	20.6	23.7	17.4	17.6	26.2	26.2	23.7	23.3
Asphaltenes	29.9	27.7	27.8	28.1	26.7	26.2	26.6	25.3
Preasphaltenes	25.8	25.1	31.2	29.0	19.4	18.1	23.3	24.7

Prince coal (batch D) used for run no. 3110-3118, inclusive
Coal concentration in feed slurry; 30 wt %

Lingan coal (batch K) used for run no. 3122-3129 inclusive
Coal concentration in feed slurry; 30 wt %

Table 6 – Product distributions from continuous experiments with Prince, Lingan and No. 26 colliery coals

Run no.	3119	3120	3131	3132	3133	3134	3135	3136
Coal tested:	Prince batch C		Lingan batch J		Lingan batch I		No. 26 batch B	
Temperature, °C	460	450	460	460	460	460	460	460
Back pressure, MPa	17.24	17.24	17.24	17.24	20.68	20.68	20.68	20.68
Slurry feedrate, kg/hr	1.022	1.025	1.029	1.007	1.072	1.005	1.031	0.995
H_2 consumption, wt % maf coal	1.5	1.1	1.8	1.5	1.5	1.2	1.3	1.1
Conversions, wt % of maf coal								
Pentane solubles plus gases	47.3	45.1	47.0	45.1	41.8	44.0	36.3	37.0
Benzene solubles plus gases	73.7	70.5	71.7	71.3	67.3	68.9	61.4	62.8
THF solubles plus gases	87.1	86.5	89.4	88.9	87.0	87.7	85.1	85.7
Product distribution, wt % of maf coal								
C_1-C_2	8.3	5.9	8.0	8.6	7.7	7.6	7.5	7.9
C_3	4.2	3.1	3.5	3.6	3.0	3.2	2.9	3.1
C_4	2.7	2.6	2.8	3.1	2.9	3.8	3.6	3.4
NH_3, H_2O, H_2S, CO_x	4.8	4.0	3.1	3.3	2.0	2.4	1.3	1.5
Oil	27.3	29.5	29.6	26.5	26.2	27.0	21.0	21.1
Asphaltenes	26.4	25.4	24.7	26.2	25.5	24.9	25.1	25.8
Preasphaltenes	13.4	16.0	17.7	17.6	19.7	18.6	23.7	22.9

Coal concentration in feed slurry; 30 wt %

Table 7 – Catalytic hydrogenation of Lingan coal at medium severity operating conditions

Run no.	5005	5006	5007	5009	5010	5011	5012	5014
Temperature, °C	460	460	460	451	451	451	467	455
Back pressure, MPa	17.24	17.24	17.24	17.24	17.24	17.24	17.24	17.24
Slurry feedrate, kg/hr	1.054	1.009	0.793	0.925	0.925	0.942	0.927	1.319
H_2 treatrate, wt % dry coal	7.5	8.0	15.1	11.0	14.9	12.8	13.0	13.0
Catalyst level, wt % maf coal	4	8	8	7	7	10	8	8
H_2 consumption, wt % maf coal	4.0	4.3	5.6	4.1	4.8	4.0	4.8	4.3
Conversions, wt % of maf coal								
Pentane solubles plus gases	45.0	50.2	60.1	50.7	51.2	52.5	59.7	49.0
Toluene solubles plus gases	76.8	79.8	84.6	79.7	79.5	80.6	84.9	77.0
THF solubles plus gases	91.0	90.9	91.6	91.4	91.6	91.2	92.1	90.5
Product distribution, wt % of maf coal								
C_1-C_2	6.9	7.7	9.8	6.5	6.7	6.8	11.0	6.4
C_3	2.8	3.2	3.8	2.6	2.6	2.5	4.5	2.4
C_4	2.4	2.6	3.3	2.4	2.6	2.7	3.8	2.7
NH_3, H_2O, H_2S, CO_x	3.0	3.6	5.0	2.7	4.6	4.4	5.8	4.4
Oil	29.9	33.1	38.2	36.5	34.7	36.1	34.6	33.1
Asphaltenes	31.8	29.6	24.5	29.0	28.3	28.1	25.2	28.0
Preasphaltenes	14.2	11.1	7.0	11.7	12.1	10.6	7.2	13.5

Run no.	5015	5016	5017
Temperature, °C	455	460	460
Back pressure, MPa	17.24	17.24	17.24
Slurry feedrate, kg/hr	0.926	0.858	0.882
H_2 treatrate, wt % dry coal	12.0	14.0	12.2
Catalyst level, wt % maf coal	8	8	8
H_2 consumption, wt % maf coal	4.1	4.4	3.7
Conversions, wt % of maf coal			
Pentane solubles plus gases	52.6	55.9	60.9
Toluene solubles plus gases	80.7	81.6	83.8
THF solubles plus gases	90.7	90.9	91.9
Product distribution, wt % of maf coal			
C_1-C_2	7.4	9.4	9.4
C_3	2.9	3.6	4.3
C_4	3.0	3.6	3.7
NH_3, H_2O, H_2S, CO_x	5.0	5.4	5.3
Oil	34.3	33.9	38.2
Asphaltenes	28.1	25.7	22.9
Preasphaltenes	10.0	9.3	8.1

Coal concentration in feed slurry; 29.5 wt %
Nalco NM 502 catalyst used in run no. 5005-5015 and 5017
HDS-1442 catalyst used in run no. 5016
7.5% H vehicle oil used in run no. 5005-5016
9.0% H vehicle oil used in run no. 5017

Table 8 – Conversion and product distribution data for Lingan, Prince and Illinois No. 6 coals

Run no. Coal used	5011 Lingan batch L	5018 Illinois No. 6	5019 Illinois No. 6	5020 Prince batch D	5020A Prince batch D
Temperature, °C	451	451	451	451	451
Back pressure, MPa	17.24	17.24	17.24	17.24	17.24
Slurry feedrate, kg/hr	0.942	0.936	0.953	0.922	0.915
H_2 treatrate, wt % dry coal	12.8	13.1	13.0	13.2	13.0
Catalyst level, wt % maf coal	10	10	10	10	10
H_2 consumption, wt % maf coal	4.0	5.9	5.7	4.6	5.1
Conversions, wt % of maf coal					
Pentane solubles plus gases	52.5	78.0	76.9	63.4	61.8
Toluene solubles plus gases	80.6	91.9	91.7	85.6	85.9
THF solubles plus gases	91.2	93.6	93.3	90.6	90.5
Product distribution, wt % of maf coal					
C_1-C_2	6.8	5.7	5.6	7.1	6.4
C_3	2.5	2.8	2.9	2.9	2.5
C_4	2.7	2.7	2.7	2.9	3.1
NH_3, H_2O, H_2S, CO_x	4.4	9.1	8.9	8.0	8.8
Oil	36.1	57.7	56.8	42.5	41.0
Asphaltenes	28.1	13.9	14.8	22.2	24.1
Preasphaltenes	10.6	1.7	1.6	5.0	4.6

Vehicle oil used: hydrogenated anthracene oil, 7.5% H
Coal concentration in feed slurry; 29.5 wt %

Table 9 – Catalytic hydrogenation of Lingan coal at increased severity

Run no.	5011	5021	5022	5023	5024	5026
Temperature, °C	451	451	460	460	460	460
Back pressure, MPa	17.24	17.24	17.24	17.24	20.68	20.68
Slurry feedrate, kg/hr	0.942	0.940	0.948	0.705	0.698	0.703
H_2 treatrate, wt % dry coal	12.8	12.6	12.3	13.0	13.0	13.0
Catalyst level, wt % maf coal	10	20	20	20	20	10
H_2 consumption, wt % maf coal	4.0	5.1	5.0	7.2	6.6	6.4
Conversions, wt % of maf coal						
Pentane solubles plus gases	52.5	55.6	61.9	66.7	72.2	65.5
Toluene solubles plus gases	80.6	83.4	85.7	86.8	89.1	86.8
THF solubles plus gases	91.2	89.5	89.7	90.9	90.7	91.7
Product distribution, wt % of maf coal						
C_1-C_2	6.8	6.5	9.0	10.1	9.2	9.4
C_3	2.5	2.4	3.0	3.9	4.2	4.1
C_4	2.7	3.4	3.2	3.4	4.2	4.3
NH_3, H_2O, H_2S, CO_x	4.4	5.8	6.2	6.9	7.5	5.4
Oil	36.1	37.5	40.5	42.4	47.1	42.3
Asphaltenes	28.1	27.8	23.8	20.1	16.9	21.3
Preasphaltenes	10.6	6.1	4.0	4.1	1.6	4.9

Coal concentration in feed slurry; 29.5 wt %
Catalyst used: Nalco NM 502
7.5% H vehicle oil used in run no. 5021, 5022 and 5023
9.0% H vehicle oil used in run no. 5024 and 5026

Table 10 – Summary of results from first-stage dissolution studies

Run no.	5027	5028	5029	5030	5031	5032	5033	5034
Temperature, °C	460	460	460	440	440	460	440	440
Back pressure, MPa	6.89	10.34	6.89	10.34	6.89	10.34	6.89	10.34
Slurry feedrate, kg/hr	2.010	1.042	1.005	2.024	1.026	2.008	2.064	1.036
H_2 consumption, wt % maf coal	1.0	0.9	0.4	0.4	0.4	1.0	0.8	0.9
Conversions, wt % of maf coal								
Pentane solubles plus gases	35.0	38.5	38.7	23.7	32.0	36.0	25.3	32.0
Toluene solubles plus gases	60.8	65.2	65.5	50.8	59.3	61.7	50.5	60.3
THF solubles plus gases	83.4	84.6	83.8	82.3	83.4	84.8	81.7	84.4
Product distribution, wt % of maf coal								
C_1-C_2	6.3	9.2	9.9	3.3	5.0	6.1	3.5	5.0
C_3	2.2	3.5	3.8	1.1	1.9	2.4	0.9	1.6
C_4	2.7	3.2	3.1	2.1	2.4	2.7	1.7	2.4
NH_3, H_2O, H_2S, CO_x	3.8	3.7	4.1	2.7	3.2	3.5	2.8	3.3
Oil	20.0	18.9	17.8	14.5	19.5	21.3	16.4	19.7
Asphaltenes	25.8	26.7	26.8	27.1	27.3	25.7	25.2	28.3
Preasphaltenes	22.6	19.4	18.3	31.5	24.1	23.1	31.2	24.1

Lingan coal used for run no. 5027-5034 inclusive
Coal concentration in feed slurry; 30 wt %

Table 11 – Results of non-integrated, two-stage liquefaction trials with Lingan coal

Run no.	5035 I	5035 II	5035 I & II	5036 I	5036 II	5036 I & II	5037 I	5037 II	5037 I & II
Temperature, °C	460	390		460	430		440	430	
Back pressure, MPa	10.34	20.68		10.34	17.24		17.24	17.24	
Slurry feedrate, kg/hr	2.073	1.142		2.089	0.765		2.028	0.734	
Catalyst, wt % maf coal	0.0	10		0.0	20		0.0	20	
H_2 consumption, wt % maf coal	0.6	1.1	1.7	0.6	2.7	3.3	0.9	3.2	4.1
Conversions, wt % of maf coal									
Pentane solubles plus gases	34.8	42.7	42.7	33.8	60.4	60.4	24.1	55.6	55.6
Toluene solubles plus gases	62.0	73.7	73.7	61.3	85.7	85.7	52.0	83.5	83.5
THF solubles plus gases	84.1	89.5	89.5	84.4	90.4	90.4	84.0	89.8	89.8
Product distribution, wt % of maf coal									
C_1-C_2	6.1	1.3	7.4	5.3	3.0	8.3	3.1	3.2	6.3
C_3	2.3	0.1	2.4	2.0	0.9	2.9	1.0	0.9	1.9
C_4	2.9	2.5	5.4	2.6	2.8	5.4	2.4	2.9	5.3
NH_3, H_2O, H_2S, CO_x	3.5	0.6	4.1	3.8	3.4	7.2	2.7	2.5	5.2
Oil	20.0		23.4	20.1		36.6	14.9		36.9
Asphaltenes	27.2		31.0	27.5		25.3	27.9		27.9
Preasphaltenes	22.1		15.8	23.1		4.7	32.0		6.3

Coal concentration in feed slurry; 30 wt %
Nalco NM 502 catalyst used in run no. 5035 II, 5036 II and 5037 II
9% H vehicle oil used in run no. 5035 I, 5036 I and 5037 I

FIGURES

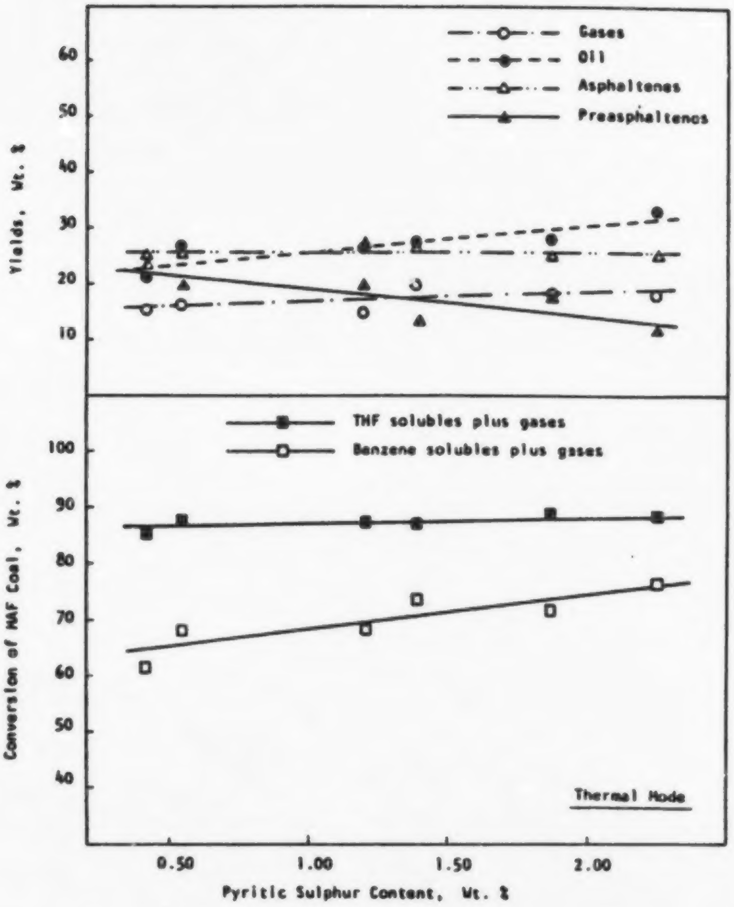

Fig. 1 – Influence of pyritic sulphur content on coal conversion

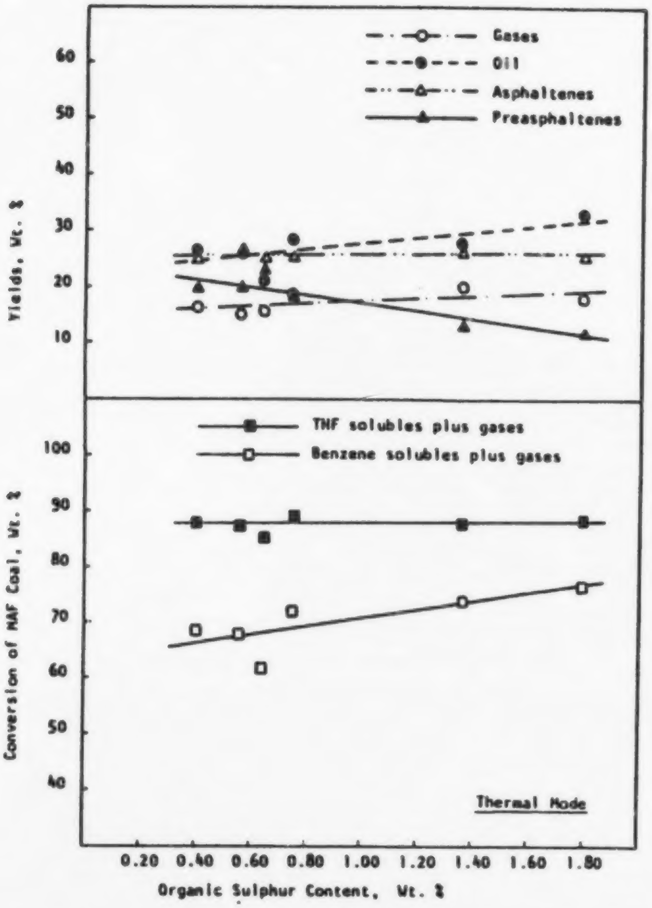

Fig. 2 – Coal conversion as a function of organic sulphur content

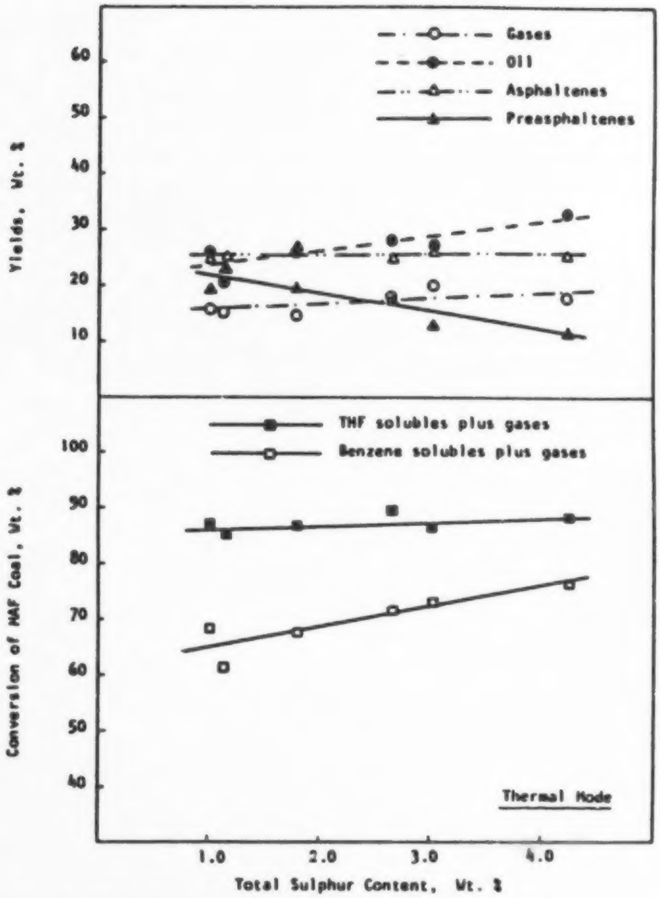

Fig. 3 – Variation of coal conversion with total sulphur content

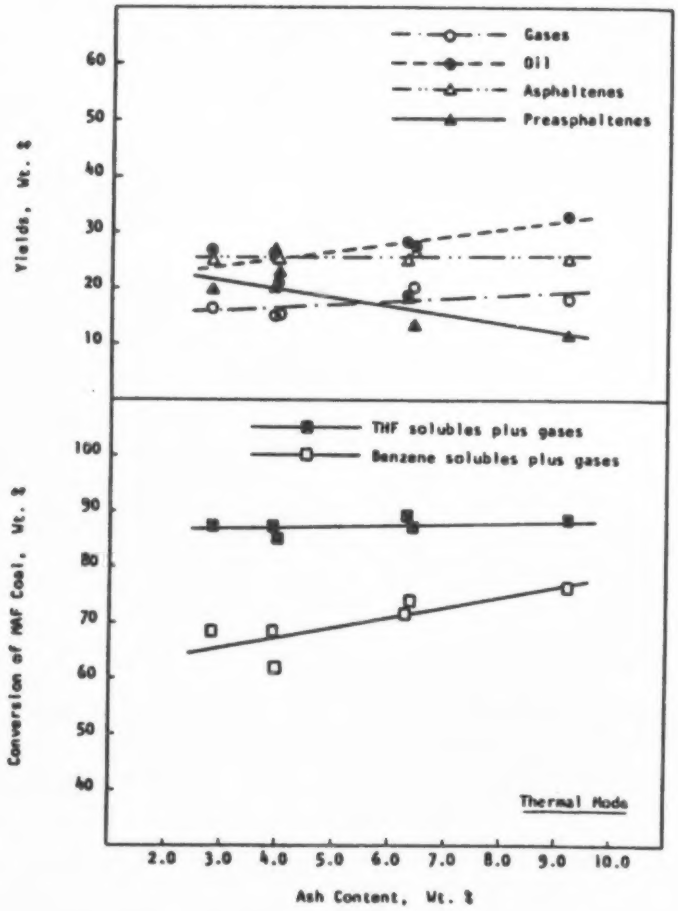

Fig. 4 – Effect of ash content on coal conversion

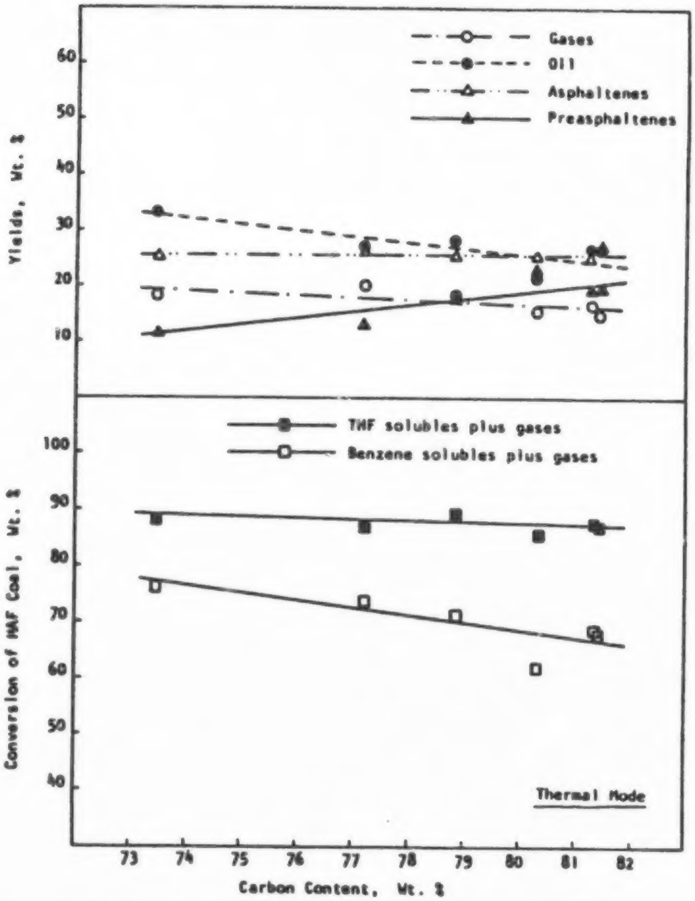

Fig. 5 – Influence of carbon content on coal conversion

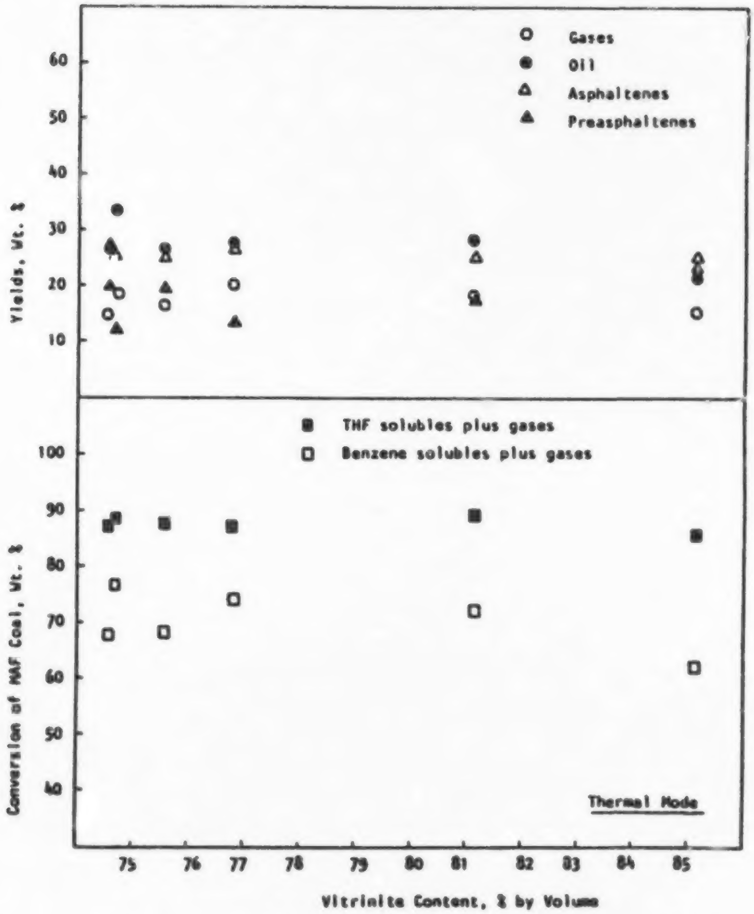

Fig. 6 – Variation of coal conversion with vitrinite content

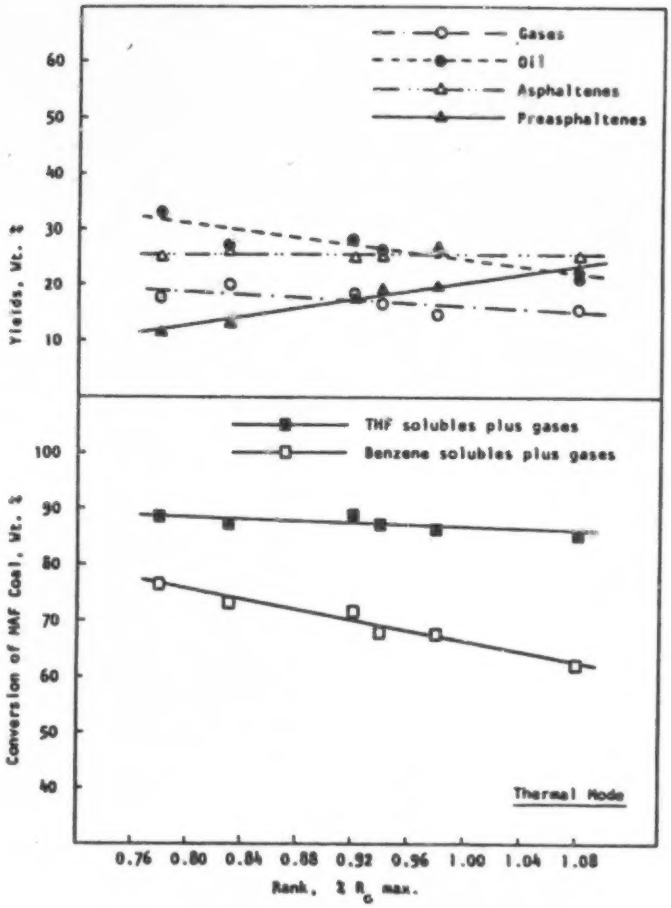

Fig. 7 – Effect of rank on coal conversion

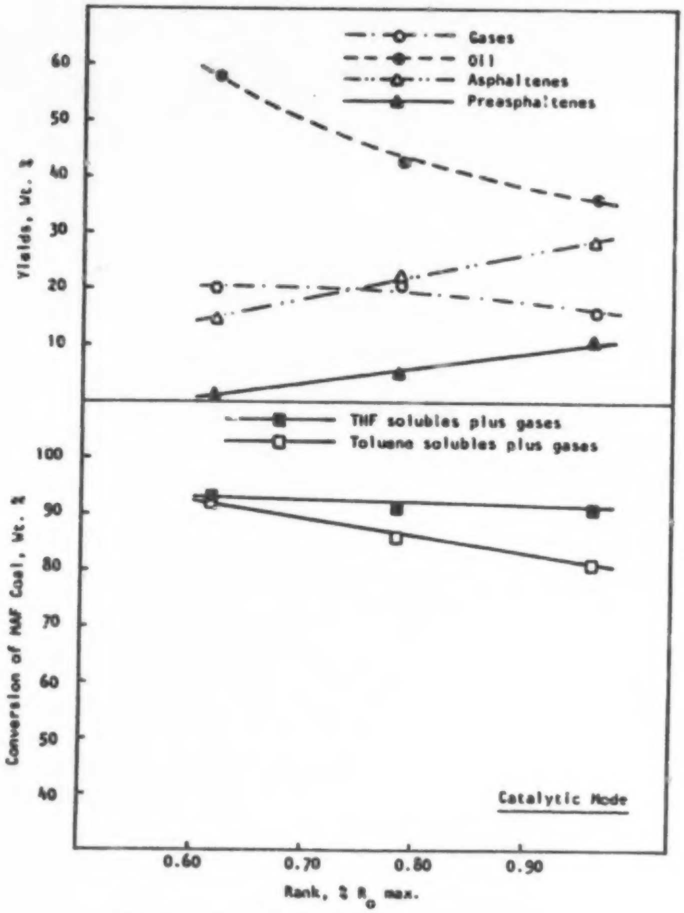

Fig. 8 – Effect of rank on coal conversion

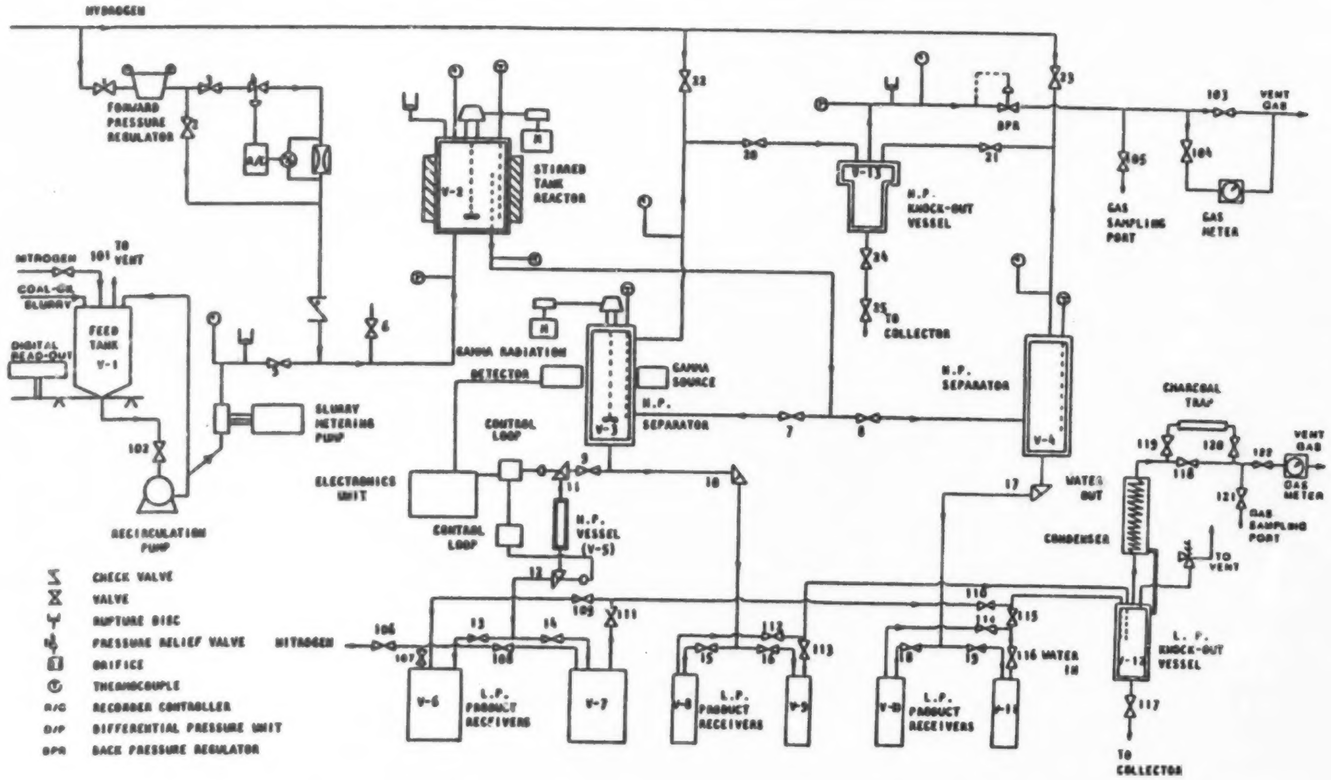
HYDROGEN
FORWARD PRESSURE REGULATOR
2
3
4
R/C
D/P
NITROGEN
101
TO VENT
COAL-OIL SLURRY
DIGITAL READ-OUT
FEED TANK V-1
102
RECIRCULATION PUMP
SLURRY METERING PUMP
5
6
V-2
STIRRED TANK REACTOR
R
22
GAMMA RADIATION DETECTOR
GAMMA SOURCE
H.P. SEPARATOR
V-3
CONTROL LOOP
ELECTRONICS UNIT
CONTROL LOOP
9
11
H.P. VESSEL (V-5)
12
10
7
8
20
21
V-13
H.P. KNOCK-OUT VESSEL
24
25
TO COLLECTOR
BPR
23
103
VENT GAS
105
104
GAS SAMPLING PORT
GAS METER
H.P. SEPARATOR
V-4
17
WATER OUT
CHARCOAL TRAP
119
120
118
122
VENT GAS
GAS METER
121
GAS SAMPLING PORT
CONDENSER
TO VENT
110
114
115
116
WATER IN
V-12
L. P. KNOCK-OUT VESSEL
117
TO COLLECTOR
NITROGEN
106
107
13
108
14
109
111
V-6
L.P. PRODUCT RECEIVERS
V-7
112
15
16
113
V-8
L.P. PRODUCT RECEIVERS
V-9
18
19
V-10
L.P. PRODUCT RECEIVERS
V-11
CHECK VALVE
VALVE
RUPTURE DISC
PRESSURE RELIEF VALVE
ORIFICE
THERMOCOUPLE
R/C RECORDER CONTROLLER
D/P DIFFERENTIAL PRESSURE UNIT
BPR BACK PRESSURE REGULATOR

Fig. 9 – Flowsheet for continuous coal liquefaction unit

SESSION I

DISCUSSION

MODERATOR: M.M. PAPIC, B.C. HYDRO

YAN (MOBIL): I would like to make a few comments on this morning's session and try to share some ideas with you and would appreciate your comments in return. Over ten years ago, I had the job of looking after the coal conversion processes and in looking at the use of non-petroleum resources as an energy source at Mobil Oil Corporation. At that time, to make a long story short, I was overwhelmed by the fact that in coal conversion the process cost is really very large. The cost of the coal itself is a very minimal amount of the total cost of the product. This is particularly true in U.S. economics; I don't know what the situation is in Canada. Because of this I came to the immediate conclusion that if you are to do coal conversion, whatever product you want to make, the first order of business is to choose the best coal, regardless of the cost of the coal. Now this morning, I was surprised to find that here we are all looking at a very low-quality coal, a very poor coal by U.S. standards. We are working very hard on it, which is good for the human being as a whole, but I think we are making our job extremely difficult. Now a second question is, if in a province we have this resource, just like a company has this resource, what are we going to do with it? Generally, I would choose less cost-intensive processes. In my opinion, I don't want to choose the most cost-intensive process such as coal liquefaction. I was very impressed with Dr. Mikhlin struggling very hard to upgrade a low-quality lignite so that you can fit it into a cost-intensive process, and I wish him a very successful upgrading process. I think I should stop here, so we can develop more discussion. In fact, I have developed some criteria to relate a process to a coal, or the other way around, what is the coal value if we are to make something or to use it in what kind of process? I hope I can publish this shortly with the permission of Mobil.

McELROY (B.C. RESEARCH): In many senses I would agree with Dr. Yan's comments. Certainly process cost is a key component. I guess my reaction is that I would like to turn it around to Mobil and similar process-oriented companies and say we are limited by what God gave us in our resources. Can't you find us a cheaper process? In terms of operating on the best coal, I'd just like to comment specifically on the B.C. scene. I pointed to it on the map this morning. The Bowren River deposit in British Columbia is potentially a lovely feedstock for coal liquefaction. It is very high in vitrinite, either low in ash or very readily washable, and gives very high conversions and very high oil yields. This is published information. Unfortunately, mining costs in Canadian dollars (depending on whether you believe the optimists or the pessimists) are in the $90 to $120 per ton range. Again you need a cheap process if you are going to compete with today's hydrocarbon fuel prices, because you have only about $2.00 a gigajoule to convert it from a very pretty solid to a runny liquid.

MIKHLIN (SNC): First of all, I would agree that the best thing is to have high quality and cheap coal. Unfortunately, we don't have this possibility. At the same time, in Canada, as well as in other countries, there is a huge amount of not very good coal (which is lignite) and at the same time it is not very good because it's very young coal (only 5 million years old). What we are trying to do is to upgrade this coal cheaply which is definitely a difficult task. But we have had up to this point, quite promising results. The idea as I think it was presented (without elaborating on how we are doing this) is to use the same oil which is already required for the process. That means to write off the cost of oil and most of the grinding costs. That is the situation. Now, the agglomeration process itself is very expensive. As you likely know, in Germany there was a semi-commercial or commercial plant working for a number of years with excellent results. The plant was shut down for economic reasons when oil agglomeration was used as such for separate beneficiation. In our approach where the oil really does not cost us anything, because it is required for the process, we see a way for cheap beneficiation and to use what is available in large quantities. By definition a surface-mined coal is cheap, and that is what we are trying to do.

On this occasion, I would also like to acknowledge that for our research we have had the privilege of CANMET funding. I would also like to acknowledge the very good cooperation we got from the U.S. Department of Energy in supplying us with samples of various coal-derived oils. At this time, we all know that very few coal liquefaction facilities are still operating.

SCOTT (UNIV. OF WATERLOO): I would like to ask Dr. McElroy what is the source of the carbon dioxide for Hat Creek coal. Is this from the organic matter of the coal or from the mineral matter or partly both? And also, it was mentioned that in the approximate analysis there were volatiles in addition to water. What were they?

McELROY (B.C. RESEARCH): Well, our assumption is, in the absence of a lot of detailed chemistry, that the carbon dioxide originates from oxygen in the organic component of the coal. Regarding sperious contributors to volatile matter; normal moisture I don't regard as a sperious contributor. We drive that out as part of the procedure. There is chemically bound water in the structures of the clay, which is the principal component of the ash. That's the major one in this particular coal. There are quite a number of others in other coals like carbonates, both dolmite and calcite which give up their carbon dioxide over the temperature interval where you do volatile matter analysis. That's an initial outline. Other than that you have to look at the mineralogy of the coal.

SCOTT (UNIV. OF WATERLOO): I guess I was really asking specifically, do these occur from the Hat Creek coal?

McELROY (B.C. RESEARCH): For Hat Creek it's the structural water of the clay, which if you were processing it as a clay for alumina from clay, you would calcine at 800°C. That's where the bulk of it comes off.

SCOTT (UNIV. OF WATERLOO): Dr. Mikhlin, I didn't quite understand your reasoning as to why the Lurgi-Ruhrgas pyrolysis process was discarded in your economic evaluation. In fact, Lurgi has done a complete economic analysis that I know of for these processes coupled to char-using industries of one kind or another.

MIKHLIN (SNC): The project objectives (which were set by the Saskatchewan Coal Liquefaction Committee) were to look at the processes from one restricted point of view, that is, for production of liquid products only. Char evaluation was not included as an objective for this study. That's why the Lurgi-Ruhrgas process, which seems to be very interesting as a route for liquefaction and char production, was not included in further techno-economic evaluations.

Also, if Lurgi, as the process developer, consider that based on a Fischer assay the expected liquid product yields will be less than 10%, then they do not consider such a coal suitable for production of liquid products from pyrolysis. This was also one of the reasons why it was not included in the second phase.

CLARK (ALBERTA RESEARCH COUNCIL): I would like to ask a couple of questions if I may. First, one to Dr. McElroy concerning the mineralogy of the coal. You didn't talk a great deal about catalysis in the liquefaction of Hat Creek coal. I wondered if you had looked into the mineralogy with respect to suitable catalysts within the coal itself?

McELROY (B.C. RESEARCH): I guess my answer to that is, not really. We did look at added catalysis by ion exchange of ferrous sulphate solution. In fact, that was how we happened on the laboratory desliming beneficiation. In the first pass at that work, it looked like ion-exchanged iron was really doing a lot for us, but on a more detailed examination, that didn't really stand up. On a preliminary evaluation reducing the ash content from 35% down to about 25% (or in a similar ratio on the other coal) really didn't seem to make a significant difference in conversion, within the level of accuracy of our work. However, bear in mind that the balance of the mineral matter in this coal is largely very finely dispersed, almost matrix or inherent ash mineral. Whether in fact that is catalytically active or not, I'm really not sure.

CLARK (ALBERTA RESEARCH COUNCIL): OK, thank you. I'd like to address a question to Dr. Starzomski about the Cape Breton coals. You described the hydrocarbon gasification levels. What about CO_2 production and CO production for these particular coals?

STARZOMSKI (N.S. RES. FOUND. CORP.): The more detailed analyses of gases are actually given in the paper. The levels of carbon oxides are very low with this coal, normally less than 1%. The major hydrocarbon gases (C_1 to C_4) comprise the bulk of the gas make.

KELLY (CANMET): I'd like to ask Joe Starzomski a question. I've heard speculation that for the Scotia Synfuels project to be economic, liquid yields of somewhere about 5 barrels per ton are required. Based on your experimental results with Nova Scotia coals, do you think this is feasible?

STARZOMSKI (N.S. RES. FOUND. CORP.): I think I'd be more prepared to answer that question when we have an opportunity to look at the two-stage approach. Based on our data on conventional single-stage catalytic liquefaction, yields of 5 barrels per ton are outside the realm of possibility.

KELLY (CANMET): I have a second question for Joe Mikhlin or maybe Stephen Hodd. Joe, you talk about removing mineral matter before processing and Stephen talks about taking it out after processing. Are there advantages for a given coal or a given process to either of the routes? Where do we stand? If we had to choose today, say as part of a concentrated research effort, what would be the approach that we should use?

MIKHLIN (SNC): It seems to me (and I think this point of view is shared by most of the process developers worldwide) that if it's possible to remove ash prior to liquefaction, and to do it cheaply, than that's the way to go. In any case, in order to remove solids within the process you have to use a substantial amount of product which you cannot avoid, whatever method you are using. That's why the important question is how cheap is it possible to make beneficiation? In the case of the concept I presented here, we definitely think that this is the way to go, especially if our promising results are further confirmed on a larger scale or by more extensive experiments. In this case, we are really not paying for the oil, or the grinding. If that's possible, that's the way to go. So, I would think, all possible effort should be made to reduce the ash as much as possible by beneficiation if it is economically viable, and then definitely one should look for the most suitable method for reducing ash content further within the process. But to use high ash coal for direct liquefaction, it is really very questionable if it is viable. I would not dare suggest using direct liquefaction, at least for high ash coal, whatever method is used within the process.

HODD (SBRG): I guess our views on it are that perhaps there are complementary technologies. We've demonstrated successful de-ashing with up to 20% ash. I'm not sure how effective it would be with higher levels of ash. I think it still would be. The other thing though, is that in beneficiation if you are successful in taking out ash you still have the problem of taking out the unreacted coal fractions. There are two types of solids. There is the ash and there is the unconverted coal. The ash is basically the easier part to take out in a de-ashing process mainly because of its higher specific gravity relative to the products. So there is still a need to take out those solids which are unreacted coals. These still represent a material that takes with it some of the valuable product. So we don't see that even high efficiency beneficiation in the front end eliminates a need at some point in the process for an efficient de-ashing step. However, the corollary may not be necessarily true with many coals. We think that it may not be necessary to give a high degree of beneficiation, particularly if you can remove all the ash and the unreacted coal out of the process at a very early stage. We had some tests which showed that we could do that even with material that had only been passed through a preheater for a very short period of time.

duPLESSIS (ALBERTA RESEARCH COUNCIL): Dr. Mikhlin, I note in your abstract that for the tests done by the U.K. National Coal Board, on I believe Onakawana lignite, you claim that these tests indicated 87-90% liquid yields. Is that number correct?

MIKHLIN (SNC): Yes, this number is correct, but it is not liquid yield, it is coal conversion to liquid and gaseous products on a maf basis. The results of the NCB showed that for Onakawana lignite it was 90%, for Willowbunch lignite it was 65%.

duPLESSIS (ALBERTA RESEARCH COUNCIL): So the abstract then refers to total coal conversion?

MIKHLIN (SNC): Yes, that's right.

duPLESSIS (ALBERTA RESEARCH COUNCIL): What would be the liquid component of that total conversion?

MIKHLIN (SNC): Well, I don't remember the number by heart, but I think it is something like 55%.

duPLESSIS (ALBERTA RESEARCH COUNCIL): I would suggest that a correction be made in the abstract.

MIKHLIN (SNC): Well, in the paper the actual figures are presented, so there are corrections, if they are needed.

VANCEA (OERD/EMR): I have a question for Dr. Mikhlin. Would you comment on the quality of liquids that you obtained by direct and indirect liquefaction?

MIKHLIN (SNC): Well in the report there is quite a comprehensive presentation on quality of the products from the direct and indirect liquefaction routes. These data are based on those supplied by the process developers. As it is quite well known, the gasoline and diesel fuels from the indirect coal liquefaction route are compatible with the specifications for similar products from petroleum. However, it is also known that, for example, gasoline from Mobil MTG has some differences from standard gasoline from petroleum. Now, data on the quality of products from direct liquefaction processes showed that upgrading to gasoline or diesel fuel could be done with existing refining processes for upgrading. There is also substantial data on gasoline from LSE naphtha or EDS naphtha and tests have showed that the quality of products is quite suitable for use as a blending stock. Also, in connection with diesel fuels from mid-distillate, it has been shown that using some chemicals in order to have diesel characteristics correspond to standard petroleum characteristics gave positive results. But I think in order to answer your question more comprehensively, it would be better to review the data presented in the report which are quite comprehensive.

SESSION II

INTERNATIONAL COOPERATION

Chairman: M.P. duPlessis

SESSION II: PAPER 6

CANADIAN PARTICIPATION IN JOINT INTERNATIONAL COAL CONVERSION ACTIVITIES

*I.C.G. Ogle**
Office of Energy Research and Development
Department of Energy, Mines and Resources

ABSTRACT

The general mechanisms for initiating joint international cooperation in R&D on a government-to-government basis are described. Umbrella Science and Technology Agreements, the principal mechanism, are explained with particular emphasis on the potential role of private industry, and the agreements under which Canada participates in R&D with other countries are reviewed.

Current status reports are presented for existing joint international coal liquefaction R&D conducted under Science and Technology Agreements, in particular, those with Japan and the Federal Republic of Germany.

Opportunities are also identified for joint coal liquefaction or conversion R&D with France, the United Kingdom and the United States. Specifically, components of the respective coal liquefaction or conversion R&D programs within these countries are highlighted, especially those programs for which international cooperation is welcomed.

**denotes speaker*

PRÉSENTATION 6

LA PARTICIPATION CANADIENNE AUX ACTIVITÉS INTERNATIONALES MIXTES RELIÉES À LA CONVERSION DU CHARBON

*I.C.G. Ogle**
Bureau de recherche et développement énergétiques
Ministère de l'Énergie, des Mines et des Ressources

RÉSUMÉ

Cette communication décrit les mécanismes généraux qui permettent les initiatives en matière de coopération internationale mixte, dans le domaine de la R-D, au niveau des gouvernements. Les accords cadres relatifs à la science et à la technologie, le principal mécanisme, sont expliqués en attachant une attention particulière au rôle possible de l'industrie privée et les accords de R-D auxquels le Canada participe, avec d'autres pays, sont examinés.

Des rapports d'étape sont présentés relativement aux travaux R-D courants entrepris en coparticipation au niveau international, visant la liquéfaction du charbon, réalisés dans le cadre d'accords sur la science et la technologie, conclus notamment avec le Japon et la République fédérale d'Allemagne. Les possibilités sont également identifiées en ce qui a trait aux travaux de R-D sur la liquéfaction ou la conversion du charbon, susceptibles d'être entrepris avec le concours de la France, du Royaume-Uni et des États-Unis. Les composantes des divers programmes de R-D sur la liquéfaction ou la conversion du charbon, dans ces pays, sont précisées, notamment les programmes pour lesquels la coopération internationale serait avantageuse.

**indique le conférencier*

CANADIAN PARTICIPATION IN JOINT INTERNATIONAL COAL CONVERSION ACTIVITIES

INTRODUCTION

In his introductory remarks (1) at the previous Coal Liquefaction Contractors' Review Meeting two years ago, Dr. K. Whitham, Assistant Deputy Minister, Research and Technology, Energy, Mines and Resources, alluded to the array of liquid fuel supply options available to Canada. He indicated that the commercial viability of coal liquefaction for domestic synthetic crude production would depend strongly on the economic competitiveness of this technology compared to the alternate crude oil supply options. Recent Canadian crude oil supply and demand projections (2, 3) and estimates of future world oil prices re-emphasize the importance of achieving a competitive cost for coal-derived synthetic crudes.

The International Energy Agency (IEA) recognized that the recent recession, together with continued oil conservation measures, would at least temporarily affect government and industry support towards commercialization of coal liquefaction technologies. The IEA Coal Liquefaction Technology Review (4), completed in 1982, sought ways to maintain the continuation of technology development and hence provide the stimulus to keep coal liquefaction research teams and expertise in place. With subsequent input from the IEA Working Party on Fossil Fuels, the recommendations resulting from this review focussed on establishment of strong research and development programs among member countries for both direct and indirect liquefaction. The primary objective was to take advantage of an apparent weakening of the commercial thrust for coal liquefaction by developing new processes, optimizing existing process efficiencies and improving the cost-effectiveness of coal liquefaction technologies in general.

It has been noted by the Economic Council of Canada and by others that Canada produces only two to four per cent of the world's technology. The Department of External Affairs is currently examining ways to improve Canada's access to world technology. Current mechanisms involve the roles of science counsellors in foreign embassies and include the Catalytic Seed Fund. This fund was initiated to provide financial assistance to Canadian parties wishing to explore the feasibility of international cooperation in the various fields of Science and Technology (S&T). The framework for initiating specific projects with any one country is established through government-to-government identification of mutually attractive areas for S&T collaboration. Areas of interest to Canada are selected by considering the views of industry and provincial and federal governments.

Currently, coal liquefaction is included within the scope of bilateral S&T collaborations between Canada and Japan, the Federal Republic of Germany (FRG) and the United Kingdom (U.K.). France and the European Economic Community (EEC) have identified coal liquefaction and gasification as areas for potential cooperation. In addition, the Electric Power Research Institute is seeking participation in its Advanced Coal Liquefaction, 6 ton/day pilot plant development program at Wilsonville, Alabama.

The Canadian coal liquefaction R&D community is well positioned to participate in cooperative international S&T. While Canada does not host, at this time, any coal liquefaction process licensors, some encouraging technical developments with substantial potential economic benefits are emerging. These include, for example, the application of spherical agglomeration technology to the beneficiation of coal feedstocks prior to liquefaction, the Sandwell Centrax Deashing Process, and developments in coprocessing technology by CANMET and the Alberta Research Council. Coal liquefaction R&D expertise now resides in a wide spectrum of Canadian organizations from universities to private industry. Bench scale and continuous liquefaction facilities exist at three provincial research organizations, at Sandwell Beak Research Centre and at CANMET. Many of these organizations have taken an active part in the S&T collaborations with Japan, the FRG and the U.K.

THE CATALYTIC SEED FUND

As described by the Department of External Affairs,

> *The Catalytic Seed Fund (CSF) is designed to stimulate international collaboration in S&T that will have economic benefits for Canada. It is used to finance such essential preliminary steps to collaboration as exploratory missions and planning meetings of experts.*
>
> *In addition the CSF provides support for medium-term working visits to allow scientists to spend up to 5 months working in laboratories and research institutions in foreign countries. The CSF will also provide support to technically qualified Canadians to assist in the collection of information on emerging technologies in their host countries.*

Any proposal to the Department of External Affairs for financial assistance of the CSF must have a sponsoring department. For S&T collaborations in the area of coal liquefaction, the Department of Energy, Mines and Resources would normally be the potential sponsor.

The relevant contacts are:

Department of External Affairs: Steve Woolcombe (613) 593-5276

Department of Energy, Mines and Resources: Iain Ogle (613) 995-9351

COAL LIQUEFACTION R&D – INTERNATIONAL ENERGY AGENCY

The primary recommendation resulting from the IEA Coal Liquefaction Technology Review was that:

> *A strong research and development program for direct and indirect liquefaction should be maintained to evaluate evolutionary improvements and to seek optimum process efficiency at the next scale.*

A compilation of R&D activities, as submitted to the IEA by member countries with an interest in coal liquefaction, is reproduced in Table 1. It demonstrates an impressive breadth of R&D activity. To this list of headings one can add *Coprocessing* with significant activity now in Canada, the U.S. and the FRG.

The IEA recognized that there were a number of general areas in which collaboration could be of benefit to the participants, for example:

- continued development of two-stage liquefaction and a further understanding of both the role of nitrogen content of the recycled solvent and of methods of removing insolubles during two-stage processing;
- development of cheaper, more efficient catalysts for both direct and indirect liquefaction and the investigation of liquefaction processes especially applicable to low-rank, low-cost coals; and
- development of improved measurement and control techniques, particularly for multi-phase process streams, with a view to increasing overall process efficiency.

Further to the last-mentioned area above, a workshop is to be hosted by Norway, in late 1984. Projects on two-phase flow, which initially do not include coal and are based on the Norwegian test facility, are to be discussed.

An initiative involving potential cooperation of two or more member countries of the IEA can be one of several types: information sharing; task sharing with a common objective; and cost sharing for a jointly conducted, single project. The IEA forum in which numerous existing bilateral and multilateral agreements concerning coal have been initiated is the Working Party on Fossil Fuels. Its mandate includes coal liquefaction. At the time of writing, Dr. D.A. Reeve, CANMET, is chairman and Mr. R.D. McDonald, Alberta Energy and Natural Resources, is a Canadian representative.

BILATERAL COAL LIQUEFACTION R&D

Canada-Japan: Status Report

The origin of cooperation under the Canada-Japan S&T Consultations in the area of coal liquefaction dates to June 1980. MacDowall (5) has described in detail not only the progress of Canada-Japan cooperation up to November 1982, but also the history and status of coal liquefaction development in Japan to that date.

Phase 2 of this agreement, now in progress, is expected to continue to December 1985. The Canadian Working Group for the Canada-Japan Coal Liquefaction Program has reached agreement with NEDO representatives on the following scope for Phase 2:

1. Continuous bench-scale tests (0.1 tonne/day) of selected Canadian coals in Japan. Coals to be tested include four Alberta coals and one from Saskatchewan.
2. Autoclave tests in Japan of three Alberta coals, three British Columbia coals and one coal each from Saskatchewan and Nova Scotia.
3. Comparison of Japanese and Canadian test results for the selected coals.
4. A Resource Evaluation Study. Individual provincial agencies will assist the NEDO mission in obtaining available information on coal resources.

The progress of the Canada-Japan cooperation from November 1982 to the present is summarized below.

1982

November 8-9	Coal Liquefaction Contractors' Review Meeting, Ottawa. Presentation of Phase 1 autoclave test results by Japanese delegates.

1983

March 2-4	Visits of Mssrs. Teranishi and Otaka to Ottawa, Edmonton and Vancouver. Ottawa discussions included agreement in principle for the proposed scope of Phase 2 with an understanding that further cooperation would depend on the results of Phase 2. Discussions in Edmonton and Vancouver addressed the selection of coals, testing techniques and the Japanese proposal to send a coal resource study team to Alberta and British Columbia.
May 18	List of B.C. Coal companies and the properties which could be visited was supplied to NEDO.
June 20-25	Dr. Suzuki, Mssrs. Ikumi, Numata and Otaka visited B.C., Alberta and Saskatchewan. Final Phase 1 results and report were presented. Details of Phase 2, including selection of coal and test procedures, were agreed. Discussions were held with officials of provincial governments. The team was given a tour of the Estevan mine site.
October 16-26	Visit of Japanese resource study team to B.C. Coal properties and Roberts Bank, Alberta and Saskatchewan coal properties.

1984

January 2-14	Samples of 10 coals from Alberta, Saskatchewan and Nova Scotia were shipped to Tokyo.
March 19-20	Visits by Dr. Maekawa to the Alberta Research Council and CANMET.
Sept. 16-28	Visit by NEDO team to B.C., Alberta and Saskatchewan coal properties. Discussions were held with senior officials of provincial governments.
October 24	Telkwa, B.C. coal sample received and prepared for shipping to Japan.
November 14-16	Coal Liquefaction Contractors' Review Meeting, Calgary.

Canada-FRG: Status Report

The origin of Canada-FRG cooperation in coal liquefaction was a visit in 1981 by a Canadian delegation of provincial and federal government and industry representatives to West Germany. The itinerary included a tour of major coal liquefaction and gasification facilities. Although this tour was not successful in establishing projects of joint interest, it did provide the basis for continuing discussion and cooperation as described below.

1982

November 8-9	Discussions were held between Drs. Graeser and Kelly concerning the potential of cooperation in a coal liquefaction component R&D program.

1983

April 10-16	A Canadian delegation led by Dr. Reeve visited West Germany. The agenda included presentations by representatives of both Canada and the FRG, tours of major pilot-plant operations and a workshop. The specific purpose of the workshop was to define R&D areas of sufficient common interest to warrant development of joint projects. Eight such project areas were identified.
May 4-5	Canada/FRG S&T Consultations, Ottawa. The eight project proposals were tabled and agreed on in principle.
December 2-13	Dr. Mikhlin, SNC, visited the FRG to complete development of a joint SNC, Veba Oil proposal on "Combined Coal and Heavy Oil Processing" applied to Saskatchewan lignites and heavy oils as feedstocks.

1984

January 17	Approval in principle was reached for 50% funding support towards the joint SNC/Veba proposal under the CANMET 50/50 Energy Conversion Program, subject to balance of support being identified by SNC.
November 14-16	Coal Liquefaction Contractors' Review Meeting. Presentation of the FRG Coal Liquefaction Program by Dr. Neef.

Canada-U.K.: Status Report

The U.K. Department of Energy announced their intention, March 1983, to proceed with the definition phase for a 2.5 tonne/day Liquid Solvent Extraction pilot plant, to be located at Point-of-Ayr. Total cost was expected to be about £30 million of which capital cost was estimated at £16 million. The balance was intended to finance a three-year test program. Joint Canada-U.K. discussions held between March and September 1983 were oriented towards defining a feasible concept for Canadian participation in the L.S.E. pilot-plant development. These discussions did not identify a mutually agreeable concept.

The option for continued discussion, however, remains open. As of August 1984, two-stage liquefaction is identified as an area for potential bilateral S&T cooperation.

Canada-U.S.: Opportunity for Cooperation

Since March 1983, EPRI has been soliciting participants for the Advanced Coal Liquefaction 6 ton/day pilot-plant program at Wilsonville, Alabama. In June 1984, EPRI announced that Standard Oil Co. of Indiana had joined the project as a sponsor.

The pilot plant, initially operated in the SRC mode, has now been converted to operation as an integrated two-stage process. The process circuitry, as indicated in Figure 1, includes coal dissolution, solids separation by filtration and Kerr-McGee critical solvent deashing, and hydrotreating.

The potential financial basis for participation of private organizations at Wilsonville is indicated below. Each organization entering the program would:

- Contribute $300,000/yr for each of three years (totalling $900,000) to support the program.
- Have the right to specify a coal and/or operation for a 30-day period within the program.
- Participate in semi-annual meetings at which accomplishments will be established and future plans developed.
- Have the right to maintain on-site observers at participant's expense, subject of course to execution of secrecy agreements with technology owners (i.e., Kerr-McGee, Hydrocarbon Research, Inc.).
- Have the right to obtain product and internal process stream samples for their own analyses.
- Have no ownership rights in the data or patents resulting from the work.

Canada-France: Opportunity for Cooperation

Under a bilateral agreement to investigate potential areas of R&D cooperation, the Department of Energy, Mines and Resources undertook to solicit the national level of interest in Canada in joint Canada-France coal R&D. A description of France's coal R&D activities in 1981, including coal conversion, was circulated to relevant Canadian organizations. The Alberta Research Council and the Saskatchewan Department of Energy and Mines identified an interest in further discussion of potential cooperation on specific liquefaction and pyrolysis projects. This information together with R&D program descriptions and general coal R&D interests were provided to France, in October 1983. A response for follow-up is awaited.

Canada-EEC: Opportunity for Cooperation

The potential of cooperation with the EEC in specific areas of energy R&D is currently being examined. Although coal, and specifically coal liquefaction, have not been identified as high-priority areas for collaboration, the EEC has provided a brief description of R&D conducted in this area. Within a total coal research budget of $CDN 20.7 million, about $CDN 3.8 million is currently allocated to coal chemistry and physics and the development of new processes.

There are five projects focussing on the improvement of analytical techniques for coal and carbonaceous products. Although no details of individual projects have been provided, research related to coal liquefaction and gasification is included within this area.

CONCLUSIONS

Cooperative bilateral R&D represents a significant and identifiable component of Canada's national coal liquefaction activities. The most successful of these activities is the Canada-Japan cooperative program: Phase 2 is now underway. Although no specific projects have been initiated to date under the Canada-FRG program, efforts are continuing to identify the necessary resources for one jointly developed project. In addition, and as a direct result of the past collaborations, discussion is continuing both within and without the S&T Agreement. The objectives are to achieve agreement on common government, industrial and R&D interests and to develop further joint projects.

In view of the recommendations of the IEA, and the wide scope of coal liquefaction R&D conducted among the IEA member countries, the possibility for increased bilateral cooperation in this area may exist. Mechanisms are in place, for example the Catalytic Seed Fund, to assist participants in establishing joint projects. Specific opportunities for further bilateral coal liquefaction R&D include cooperation with the U.S., U.K., France and the EEC.

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TABLES

Table 1 – Coal liquefaction R&D activities

Activity	Country
Liquefaction	
Fundamental studies on coal liquids	AUS, J, USA
Coal dissolution studies	AUS, J, USA, CDN
Liquefaction bottom characterization	J, USA
Preasphaltene studies	USA
Behaviour of coal macerals	AUS
Mechanism of coal liquefaction	J, AUS
Indirect liquefaction	
Liquid phase methanol	D, USA
Slurry phase Fischer-Tropsch	D, USA
Slurry F-T/Mobil 2-stage process	D, USA
Catalyst development for direct synthesis	D, USA
Slurry phase F-T catalyst studies	AUS, D, USA
Zeolite based catalyst studies	D, USA
Catalyst process studies	AUS, USA
Catalyst characterization	AUS, USA
Catalyst preparation	AUS, D, USA
Organometallic catalysts	USA
Product characterization	USA
Direct liquefaction	
Direct liquefaction Technology assessment	AUS, D, J, USA, CDN
SRC technical data analysis	AUS, D, J, USA
Development of novel liquefaction techniques	CDN, J
Solvolysis – basic studies	CDN, J
Solvent treatment of coal	AUS, CDN, D, J, UK
Catalytic hydrogenation	AUS, NL
Development of coprocessing technology	CDN, D
Autoclave tests	CDN, UK
Two-stage liquefaction	
Integrated two-stage liquefaction	CDN, USA
Catalyst synthesis and testing	USA
Pyrolysis	
Flash and hydropyrolysis	AUS, B, CDN, D, S
Product upgrading	AUS, CDN, D
Char studies	AUS, CDN, D
Disposable catalysts	
Advanced research on SRC	J, USA
Enhanced catalysis by solvent improvement	USA
Low rank coal liquefaction	AUS, CDN, D, J
Catalyst and short contact time studies	AUS, D, J, CDN

Table 1 – Continued

Activity	Country
Product refining, technology development	
Refining of coal liquids	AUS, J, CDN, D, USA
Refining of synfuels	AUS, J, CDN, D, USA
Study of ebullated-bed fluid dynamics	USA
Characterization of slurry recycle and process oils	J, CDN
Rheology of coal slurries	USA
Computer modelling of liquefaction processes	USA, J
Two-stage liquefaction research	CDN, USA
Multimedia analysis of environmental control	USA
Technology for direct liquefaction	USA
Beaded liquefaction catalysts	USA
Three-phase reactor modelling	USA
Preheater design fundamentals	USA
Solvent effects in liquefaction	J, USA
Liquefaction bottoms fractionation	USA
Lubricating potential of coal tars	AUS
Components and instruments	
Hydrohoist development	
Reactor development	
Material coating for valves	USA
Coal liquefaction preheater coking	J, USA
Micro motion flowmeter and seiscor rheometer	USA
Field evaluation of doppler slurry flowmeter	USA
Development of a synthetic fuel reciprocating charge pump	USA
Mass flow measurement technical support	USA
Solid/liquid/gas phase – fraction meter	USA
Fluid seals development for coal liquefaction slurry pumps	USA
On-line process solvent monitoring by ESR technique	USA
Development of NON-intrusive PNA mass flow rate measuring system	USA
Investigation of pulsation in slurry pumping systems	USA
High-temperature packing test programme	USA
Changes to coal minerals, catalysts and reactor wall vessels during conversion	AUS
Solids separation	J, USA, CDN
Process development units	
Two-stage liquefaction	USA
Pyrolysis	AUS, B, CDN, D
Indirect liquefaction	D, USA
Direct liquefaction	D, J, UK, USA, CDN
Environmental support	
Waste water pollution	D, USA

FIGURE

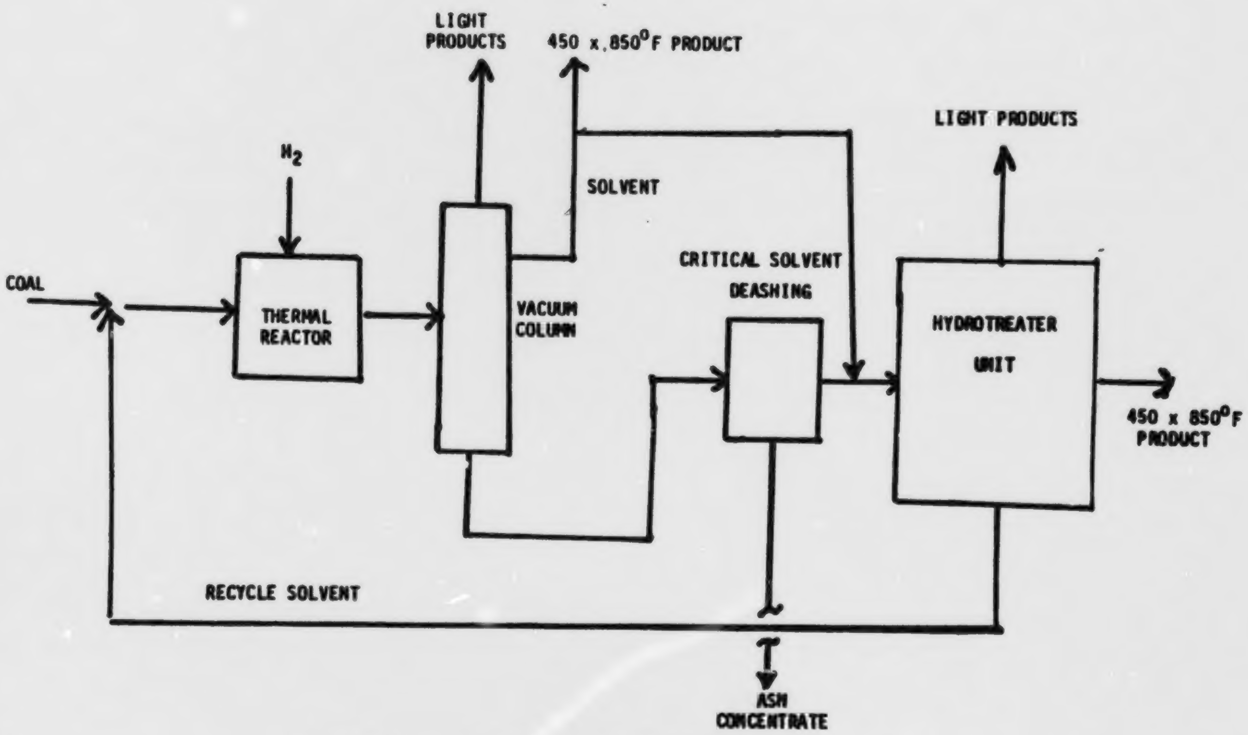
LIGHT PRODUCTS
450 x 850°F PRODUCT
LIGHT PRODUCTS
H2
SOLVENT
COAL
THERMAL REACTOR
VACUUM COLUMN
CRITICAL SOLVENT DEASHING
HYDROTREATER UNIT
450 x 850°F PRODUCT
RECYCLE SOLVENT
ASH CONCENTRATE

Fig. 1 – Schematic of Wilsonville two-stage liquefaction plant

SESSION II: PAPER 7

PRESENT STATUS OF COAL LIQUEFACTION TECHNOLOGY IN JAPAN

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ABSTRACT

The Sunshine Project, initiated in 1974, has been developing new energy technologies such as solar energy, geothermal energy, coal energy technology and so on. The Government and private sector established the "New Energy Development Organization (NEDO)" in 1980, which plays the main role in constructing and operating large-scale test plants.

Two major projects have been conducted in coal liquefaction technology: one is a bituminous coal liquefaction project, the other is a brown coal liquefaction project.

For bituminous coal liquefaction, the Japanese Government decided to develop a 250 t/d pilot plant integrating the results obtained through process development units of three different methods. The operation of the plant is scheduled in FY 1990. For brown coal liquefaction, a 50 t/d pilot plant is now under construction in Victoria State, Australia. The operation of the total plant will start in FY 1986.

The Sunshine Project has also conducted supporting R&D programs concerning coal liquefaction technology, one of which is the survey of coal resources and properties. In Phase II of the program of Canada-Japan cooperation on coal liquefaction technology, NEDO is going to carry out liquefaction tests with some Canadian coals sent by the Canadian Government.

In this paper the present status of coal liquefaction technology in Japan and the method of experiment on Canadian coal are described.

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*denotes speaker

PRÉSENTATION 7

ÉTAT ACTUEL DE LA TECHNOLOGIE DE LA LIQUÉFACTION DU CHARBON AU JAPON

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RÉSUMÉ

Le projet Soleil, lancé en 1974, permet l'élaboration de nouvelles technologies énergétiques faisant appel à l'énergie solaire, à l'énergie géothermique, au charbon et à d'autres formes d'énergie. En 1980, le gouvernement et l'entreprise privée ont crée la "New Energy Development Organization (NEDO)", un organisme qui joue le rôle principal dans le domaine de la construction et de l'exploitation des installations d'essai sur une grande échelle.

Deux grands projets reliés à la technologie de la liquéfaction du charbon ont été entrepris: un projet de liquéfaction du charbon bitumineux et un projet de liquéfaction du charbon brun.

Dans le cas de la liquéfaction du charbon bitumineux, le gouvernement japonais a décidé de construire une usine pilote de 250 t/j, qui doit intégrer les résultats obtenus grâce à des installations de mise au point de procédés faisant appel à trois méthodes différentes. L'exploitation de l'usine est prévue pour AF 1990. Dans le cas de la liquéfaction du charbon brun, une usine pilote de 50 t/j est actuellement en construction, dans l'Etat de Victoria, en Autralie. L'exploitation de toutes les installations commencera en AF 1986.

Le projet Soleil à également permis la réalisation de programmes de R-D de soutien, reliés à la technologie de la liquéfaction du charbon, dont l'un visait notamment l'inventaire des ressources et des réserves de charbon. Dans le cadre de la Phase II du Programme de coopération Canada-Japon sur la technologie de la liquéfaction du charbon, la société NEDO entreprendra des essais de liquéfaction en utilisant certains charbon canadiens expédiés par le Gouvernement du Canada.

Cette communication décrit le statut actuel de la technologie de la liquéfaction du charbon au Japon ainsi que la technique d'essai du charbon canadien.

**indique le conférencier*

PRESENT STATUS OF COAL LIQUEFACTION TECHNOLOGY IN JAPAN

INTRODUCTION

Japan's level of dependence on oil is the highest among the industrialized nations. Thus, it is Japan's urgent task to promote the development and introduction of oil alternative energies. In order to develop the technologies for producing oil alternative energies such as solar energy, geothermal energy, and coal conversion, the Sunshine Project was inaugurated in 1974 (just after the first oil crisis in 1973) by the Agency of Industrial Science and Technology, Ministry of International Trade and Industry.

The New Energy Development Organization (NEDO) is a government body which was established in 1980 to continue and advance the Sunshine Project. With considerable assistance from the private sector, NEDO is now performing various activities in this area. Among them NEDO places a specific stress on the development of coal liquefaction and gasification technology. Coal is considered to be the most promising alternative energy source because of the huge deposits that are available throughout the world.

Table I shows NEDO's present activities in coal liquefaction technology. There are three projects in this area: the Brown Coal Liquefaction Project, the Bituminous Coal Liquefaction Project and the supporting research for both liquefaction projects. These are explained in more detail in the following sections.

BROWN COAL LIQUEFACTION PROJECT

At the Japan-Australia Energy R&D Conference held in November 1980, it was decided to construct a brown coal liquefaction pilot plant near Morwell coal field in Latrobe Valley, Victoria State, as a Japan-Australia government project. This project was appointed as one of the Sunshine Projects in 1981.

Figure 1 shows the Japan-Australia joint R&D organization. NEDO is the principal developer and it has entrusted the actual implementation of the 50 t/d (daf base) pilot plant to the Nippon Brown Coal Liquefaction Co. Ltd. (NBCL), composed of five Japanese companies. The pilot plant is now under construction at the site of a subsidiary of NBCL, named Brown Coal Liquefaction Victoria Pty. Ltd. (BCLV) with the cooperation of the Victoria Brown Coal Council (VBCC). All the funds of this project are provided by NEDO.

Australia's contributions to this project are:

- supply of feed brown coal
- provision of the pilot-plant site with utility services such as water and electricity up to the boundary limits
- provision of staff employees.

Figure 2 shows the schedule for the Brown Coal Liquefaction Project. The construction of the pilot plant is divided into two stages. The first stage is to build the primary hydrogenation process and related facilities, and the second stage is deashing and the secondary hydrogenation process.

At present the installation of the primary hydrogenation process is nearly finished. After completion of the first-stage construction next year, various trial operations of the primary hydrogenation process will be carried out simultaneously with second-stage construction work. Upon completion of the second-stage construction in 1986, the integrated operation of the primary and secondary hydrogenation process will be started and the operation will continue for about two years.

Figure 3 shows a schematic diagram of the brown coal liquefaction pilot plant. In the dewatering unit, about 90% of water contained in the coal is removed by steam heating drier. Coal slurry is fed to the reactor through the preheater and is hydrogenated in the presence of disposable iron catalyst under the condition of 430-460°C and 100-150 atm. Residence time is about one hour. Products are distilled by atmospheric and vacuum distillation towers and then coal liquid bottom is fed to the following unit which will be installed in the second stage.

At the solvent deashing unit, coal-derived naphtha is used as the deashing solvent to separate the ash and to regulate the concentration of preasphaltene in the deashed oil. The secondary hydrogenation is performed on the fixed-bed reactor with Ni-Mo catalyst under the condition of 360-420°C and 150-200 atm.

The bottom from the secondary hydrogenation or the hydrogenated deashed oil is mixed with middle distillate produced in the primary and secondary hydrogenation and is recycled to the primary hydrogenation system as the recycle solvent. Hydrogen for this plant is produced from natural gas by steam reformer.

Bituminous Coal Liquefaction Project

Since its establishment in 1980, NEDO has been developing three different processes for the Bituminous Coal Liquefaction Project. They are Solvent Extractive Coal Liquefaction, Direct Coal Liquefaction, and Solvolysis Coal Liquefaction. Each has a PDU with a capacity of 1-2.4 t/d.

In Solvent Extraction Coal Liquefaction, coal is liquefied with hydrogen donor solvent in the presence of disposable iron dust catalyst produced from a molten iron gasifier under the condition of 400-450°C and 150-200 atm. This process can give us a higher yield of liquids.

In Direct Coal Liquefaction, coal is liquefied in the presence of synthetic high-active iron sulfide catalyst under the condition of 430-460°C and 200-250 atm. This process also shows us the same combined effect when it uses synthetic iron sulfide catalyst with hydrogen donor solvent.

Solvolysis Coal Liquefaction is the only two-stage liquefaction process and its uniqueness is that at the primary stage, coal is dissoluted under the condition of 350-450°C and 15 atm in a few minutes without any hydrogen. This process shows us that the recycle of heavy fraction of hydrogenated solvent is effective in increasing the yield of light oil.

Considering the results of these PDU operations, NEDO is going to integrate the three into a pilot plant named NEDOL or the catalytic hydroextractive coal liquefaction process. In spite of the recent strong opinion against efforts for developing oil alternative energies, the government-authorized committee concerning this area approved our plan last summer to establish a pilot plant in Japan with a capacity of 250 t/d.

Figure 4 shows our schedule for the Bituminous Coal Liquefaction Project. The basic design has been started and the operation will begin in 1990. The budget for this project is as follows:

fiscal year	***stage***	***million $***
1984-86	design	23
1986-89	construction	183
1990-92	operation	210
	total	416

Similar to our Brown Coal Liquefaction Project, NEDO will entrust the implementation of this project to the joint venture named Nippon Coal Oil Co. Ltd., which was established on October 1 this year. About ten per cent of the budget will be provided by this company.

The schematic diagram of the NEDOL process is shown in Figure 5. Coal is liquefied in the presence of gaseous hydrogen and donor solvent under the condition of 430-460°C and 150-200 atm using high-activity disposable catalyst. Residence time is about one hour and solvent ratio is 1.5-2. The recycle solvent composed of heavy fraction (538°C minus) and middle distillate (220-350°C) is hydrogenated at the solvent hydrogenation stage under the condition of 350°C and 100-150 atm in Ni-Mo catalyst fixed bed.

The liquid yield of the process is expected to be over 50 per cent, consisting of naphtha (C5 - 200°C) and middle distillate (220-350°C). Hydrogen for this process will be generated from conventional process. Solid-liquid separation will be performed at vacuum tower, and part of the residue will be tested as the feed for some types of gasifier.

This process should have high adaptability in processing from subbituminous to low-grade bituminous coal. The selection of feed coal for this pilot plant has not yet been done, but NEDO plans to use several overseas coals as the feed. Canadian coal, of course, is one of those proposed for this.

SUPPORTING RESEARCH

Besides the development of processes, NEDO is carrying out the supporting research programs which are to be considered as the common technology for both liquefaction projects. There is much variety in this research, so each part is delegated by NEDO to the most capable companies in Japan.

Reactor Materials

There is already a lot of knowledge about reactor materials as used in the petroleum refining industry. However, coal liquefaction requires severer reacting conditions and a more corrosive atmosphere than petroleum refining. In order for the process to be economical NEDO developed new reactor materials on the base of 3 Cr-1 Mo alloy steel. As a result of this development, new materials improve design stress intensity by 34% at a temperature of around 480°C compared with conventional ones and they also show excellent environmental capability. Figure 6 describes the details.

An adequate weld metal and stainless overlay technology have also been developed. Commercial scale heat experiments have been carried out to obtain the practical data of the new alloy. A forged shell 450 mm thick and with an inside diameter of 3,400 mm was manufactured from a large ingot of 250 metric tons. Table 2 shows the best composition of these reactor materials.

ASME codification and ASTM standardization that we applied were approved at each main committee. We plan to apply these materials to the forthcoming pilot plant.

Slurry Pumps

The feed slurry to coal liquefaction process is usually fed by plunger pumps. However, plunger pumps are limited in scale-up capacity, so reliable large capacity pumps have to be developed when commercial plants are considered.

NEDO has two programs for the development of slurry pumps, that is, centrifugal pumps and hydrohoist. Concerning centrifugal pumps, NEDO has decided to develop a vertical multistage centrifugal pump due to its simplicity of design and operation. At present, an experimental unit with 14 stages and 80 atm discharge pressure has been installed in the test circuit and we have just begun the test operation.

Hydrohoist is another type of large capacity feed system. It is composed of two centrifugal pumps and three chambers, each of which has two rooms separated by a float. Figure 7 shows the conceptual scheme. Coal slurry is introduced and discharged to and from a lower room according to the movement of the float, which is forced to move by non-solid-contained liquid. An experimental unit and test circuit have also been installed and test operation has started. Elemental research for materials of floats, chambers and plate valves is being continued.

Process Simulator

A process simulator is useful to estimate unit operations in process flowsheeting. There are many process simulators in the world for petroleum refining or chemical processing. However, there will be some limitations when we apply these process simulators to coal liquefaction because of the existence of solids and because of the big difference in properties between petroleum and coal-derived oil.

Thus, it is planned to develop a process simulator only for coal liquefaction in order to evaluate the process from engineering and economic points of view. This is expected to have functions such as physical properties estimation, mass and energy balance, cost evaluation and so on.

For making the basic concept of reaction models and yield estimation, a set of representative pure components was selected to represent the properties of distillate below 540°C, and the extended group contribution method was developed to evaluate a physical property for heavy distillate and SRC fractions based on their structural parameters, ultimate analysis and so on. The program of version 1 has just been inaugurated and we are carrying out trial calculations using an intelligent terminal connected with a time-sharing computer system.

Upgrading of Coal-derived Oil

Coal-derived oil contains many organic sulfur and nitrogen compounds, and it is less stable than petroleum. As the energy system in Japan is based largely on petroleum, it is most probable that coal-derived oil will be mixed with petroleum products and that the mixture has to meet standards regulating present petroleum products. Therefore, coal-derived oil must be hydrogenated to pass such criteria.

Physical and chemical property analysis of coal-derived oil and some study of deterioration mechanisms have been carried out so far, and a new five-year research program has been started this year. We are interested in the following: oil properties before and after hydrogenation, reacting conditions, catalysts, coprocessing with petroleum products, properties of mixture and so on.

It is believed that there are some difficulties in treating kerosene and diesel fraction because of its low smoke point and poor cetane number. We are going to investigate these points using bench-scale microreactor apparatuses.

Environmental Protection and Hygienes

The research program on environmental protection and hygienes of coal slurry, coal liquids, wastewater, and residue has just been started. A series of acute, subacute and chronic tests on small animals and microbes have been designed. There are two objectives of this program. One is to establish industrial hygiene by proposing some ideas for plant design and by preparing a handling manual for researchers and operators. Another objective is to obtain public acceptance by the confirmation of the safety of upgraded coal-derived oil which will be mixed with petroleum and distributed to public users.

Technology for Waste-water Treatment

Waste water from the coal liquefaction process contains ammonia, phenolic compounds, organic acids and sulfide in high concentrations. The existing technology utilized in coke production facilities can be applied to coal liquefaction waste water treatment. However, new efficient technologies are being investigated to make the process more economical. These technologies are the extraction of phenolic compounds with solid supported liquid membranes, the biological treatment with anaerobic fluidized bed and aerobic contact filter, and the wet catalytic oxidation. When this basic research yields results, they can be applied to our forthcoming pilot plant.

Survey of Coal Resources and Properties

Considering the future development of the coal liquefaction industry, it is indispensable that there are sufficient data on coal resources and properties throughout the world for Japan because of its limited deposits of domestic coal. Therefore, we have cooperative relations with China and Canada.

Concerning cooperation with Canada, the Phase II program is now being carried out under the Canada-Japan Science and Technology Consultation Agreement. In the Phase I program, ten Canadian coals – Wabamun, Ardley, Greenhills, Balmer, Willow Bunch, Estevan, Battle River, Drumheller, Smoky Tower and Pickardville – were tested in Japan. The results were announced at the previous meeting.

At present, six Canadian coals – Fox Creek, Tofield Dodds, South Swanhills from Alberta, Poplar River for Saskatchewan, Lingan Channel, and Prince Balk Channel from Nova Scotia – are being tested in the Coal Mining Research Center, Japan. Besides the analyses of these coals, five coals of the Phase I program were selected for the feed cost coal to the small-scale continuous liquefaction test units. They are Pickardville, Battle River, Drumheller, Wabamun and Estevan. The details of the planned tests are shown in Table 3. These coals will be distributed to two national laboratories, and the results will be obtained in mid-1985 and then announced.

Regarding the coal resources' survey, we must express our great thanks to you for your kind cooperation when our mission visited your country. Fortunately, we can be accumulating the necessary data with the assistance of Canada, China, U.S.A., Australia and other countries. In the final stage of this survey, a database will be established to be used in preparing not only for the pilot plant but also for commercial plants in the future.

ACKNOWLEDGEMENT

The author expresses hearty thanks to colleagues S. Ueda, M. Yoneda and Y. Otaka who provided much assistance for this paper.

TABLES

Table 1 – Activities of NEDO in coal liquefaction

1. Development of Process
   - (1) Brown Coal Liquefaction
     Pilot plant in Australia (50 t/d daf; 150 t/d raw coal)
   - (2) Bituminous Coal Liquefaction
     Process development unit (1-2.4 t/d)
       - Solvent extractive coal liquefaction
       - Direct coal liquefaction
       - Solvolysis coal liquefaction

     Pilot plant in Japan (250 t/d daf)
2. Development of Supporting Research
   - (1) Reactor materials
   - (2) Slurry pumps
   - (3) Process simulator
   - (4) Upgrading of coal-derived oil
   - (5) Environmental protection and hygienes
   - (6) Technology for waste water treatment
   - (7) The survey of coal resources and properties

Table 2 – Chemical composition of new alloys

	C	Si	Mn	P	S	Cr	Mo	V	Ti	B	Nb
Reactor metal	0.10 ~0.15	<0.08	<0.40 ~0.60	<0.015	<0.015	2.85 ~3.25	0.90 ~1.10	0.20 ~0.30	0.015 ~0.030	0.001 ~0.003	–
Weld metal	0.08 ~0.15	<0.25	0.40 ~0.60	<0.015	<0.015	2.85 ~3.25	0.90 ~1.10	0.20 ~0.30	0.015 ~0.030	–	–
Overlay metal	<0.05	<0.25	0.40 ~0.60	<0.015	<0.015	2.85 ~3.25	0.90 ~1.10	–	–	–	<0.5 >Cx10

Table 3 – Details of Canadian coal test

1. Coal analyses (July 1984 ~ Nov. 1984)

   Proximate analysis, ultimate analysis, heating value, sulfur forms, maceral analysis, reflectance analysis, hardgrove grindability index, analysis of ash, etc.

2. Autoclave tests (July 1984 ~ Jan. 1985)

   Autoclave: 500 ml

Standard conditions:	Temperature	450°C
	Pressure	9.8 MPa (Initial)
	Time	60 min
	Solvent	Anthracene oil or donor solvent
	Solvent/coal	1.5
	Catalyst	Fe_2O_3 + S

3. Continuous unit tests (Nov. 1984 ~ Aug. 1985)

   Testing unit:
   0.1 T/D (Government Industrial Development Laboratory, Hokkaido)
   0.3 kg/hr (National Chemical Laboratory for Industry)

Standard conditions:	Temperature	450 ~ 460°C
	Pressure	9.8 ~ 24.5 MPa
	Time	30 ~ 60 min
	Solvent	Anthracene oil or donor solvent
	Solvent/coal	1.5 ~ 2
	Catalyst	Fe_2O_3 + S and others

FIGURES

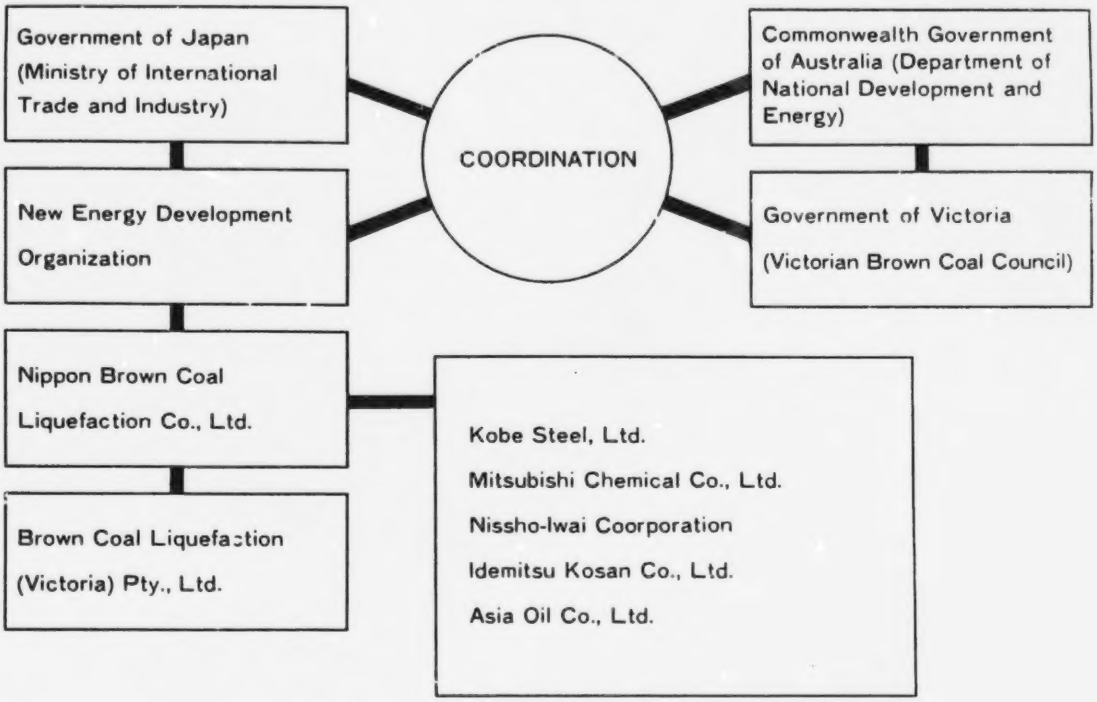
Government of Japan (Ministry of International Trade and Industry)
New Energy Development Organization
Nippon Brown Coal Liquefaction Co., Ltd.
Brown Coal Liquefaction (Victoria) Pty., Ltd.
COORDINATION
Commonwealth Government of Australia (Department of National Development and Energy)
Government of Victoria (Victorian Brown Coal Council)
Kobe Steel, Ltd.
Mitsubishi Chemical Co., Ltd.
Nissho-Iwai Coorporation
Idemitsu Kosan Co., Ltd.
Asia Oil Co., Ltd.

Fig. 1 – Development framework of Brown Coal Liquefaction Project

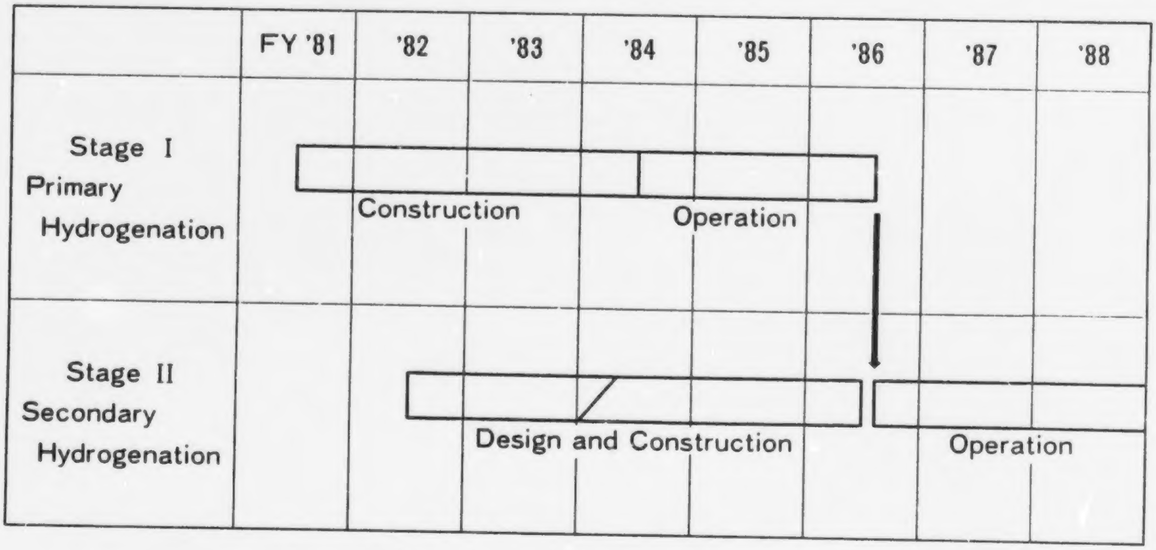

Fig. 2 – Schedule for Brown Coal Liquefaction Project

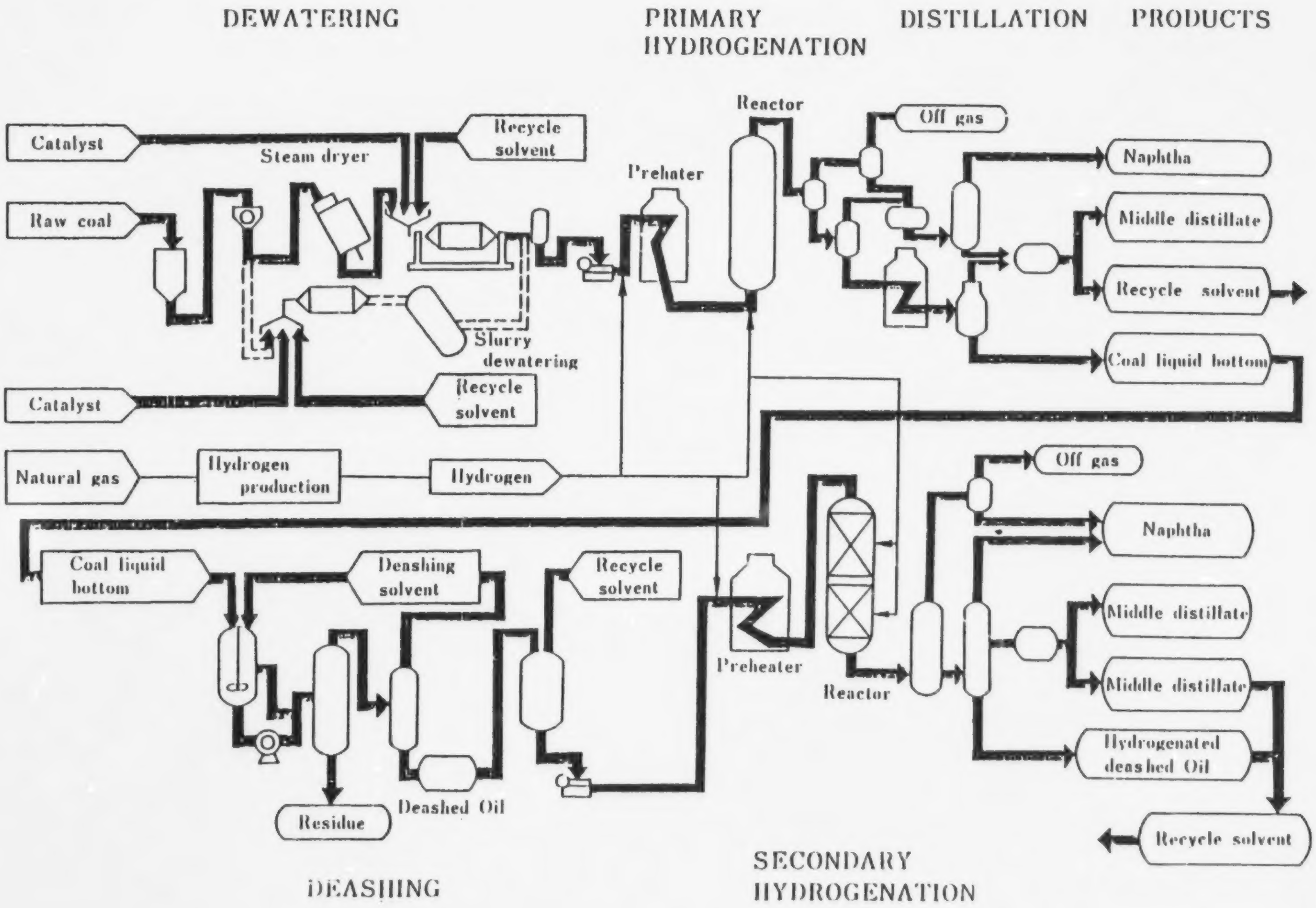
DEWATERING
PRIMARY HYDROGENATION
DISTILLATION
PRODUCTS
Catalyst
Raw coal
Catalyst
Natural gas
Steam dryer
Recycle solvent
Slurry dewatering
Recycle solvent
Hydrogen production
Hydrogen
Prehater
Reactor
Off gas
Naphtha
Middle distillate
Recycle solvent
Coal liquid bottom
Coal liquid bottom
Deashing solvent
Recycle solvent
Residue
Deashed Oil
Preheater
Reactor
Off gas
Naphtha
Middle distillate
Middle distillate
Hydrogenated deashed Oil
Recycle solvent
DEASHING
SECONDARY HYDROGENATION

Fig. 3 – Schematic diagram of brown coal liquefaction pilot plant (50 t/d)

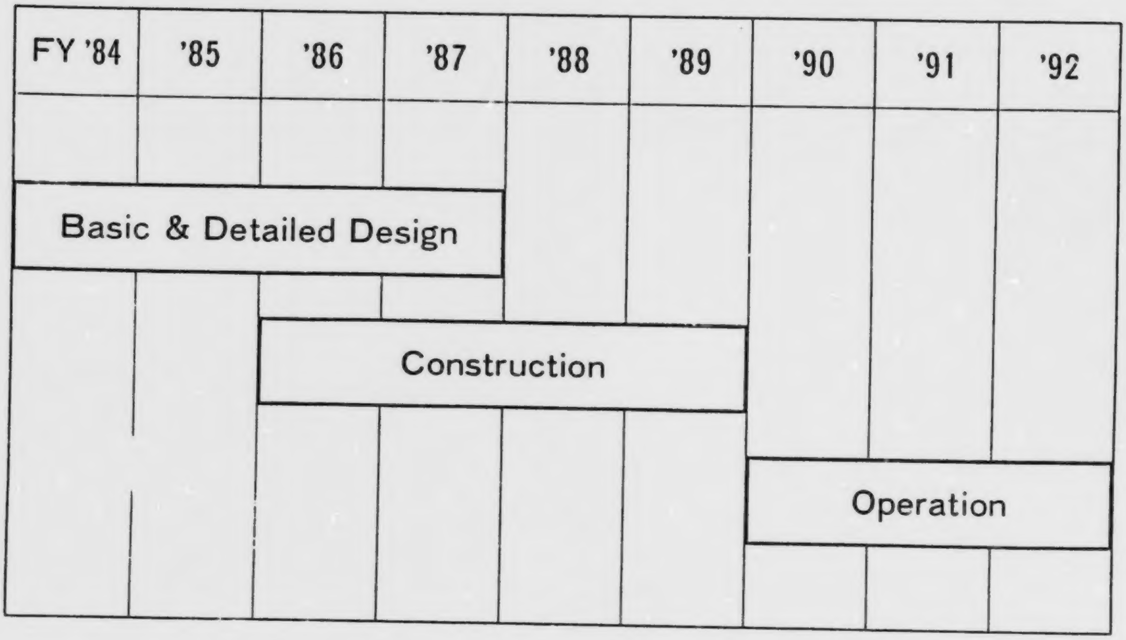

Fig. 4 – Schedule for Bituminous Coal Liquefaction Project

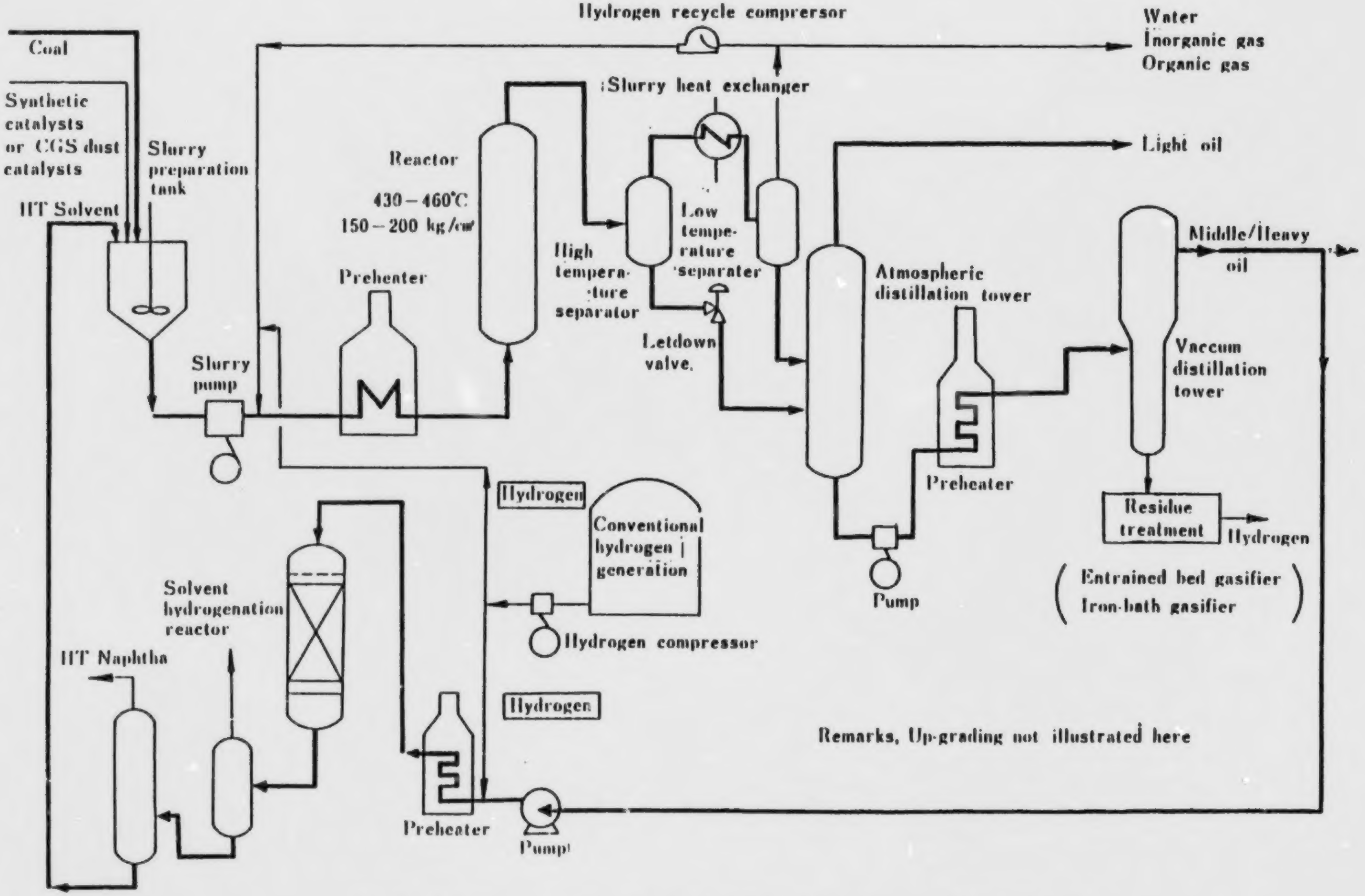
Coal
Synthetic catalysts or CGS dust catalysts
HT Solvent
Slurry preparation tank
Slurry pump
Preheater
Reactor
430 – 460°C
150 – 200 kg/cm²
High tempera-ture separator
Hydrogen recycle compressor
;Slurry heat exchanger
Low tempe-rature separater
Letdown valve.
Water
Inorganic gas
Organic gas
Light oil
Atmospheric distillation tower
Preheater
Pump
Middle/Heavy oil
Vaccum distillation tower
Residue treatment
Hydrogen
Entrained bed gasifier
Iron-bath gasifier
Hydrogen
Conventional hydrogen generation
Hydrogen compressor
Hydrogen
Solvent hydrogenation reactor
HT Naphtha
Preheater
Pump
Remarks, Up-grading not illustrated here

Fig. 5 – Schematic diagram of bituminous coal liquefaction pilot plant (250 t/d)

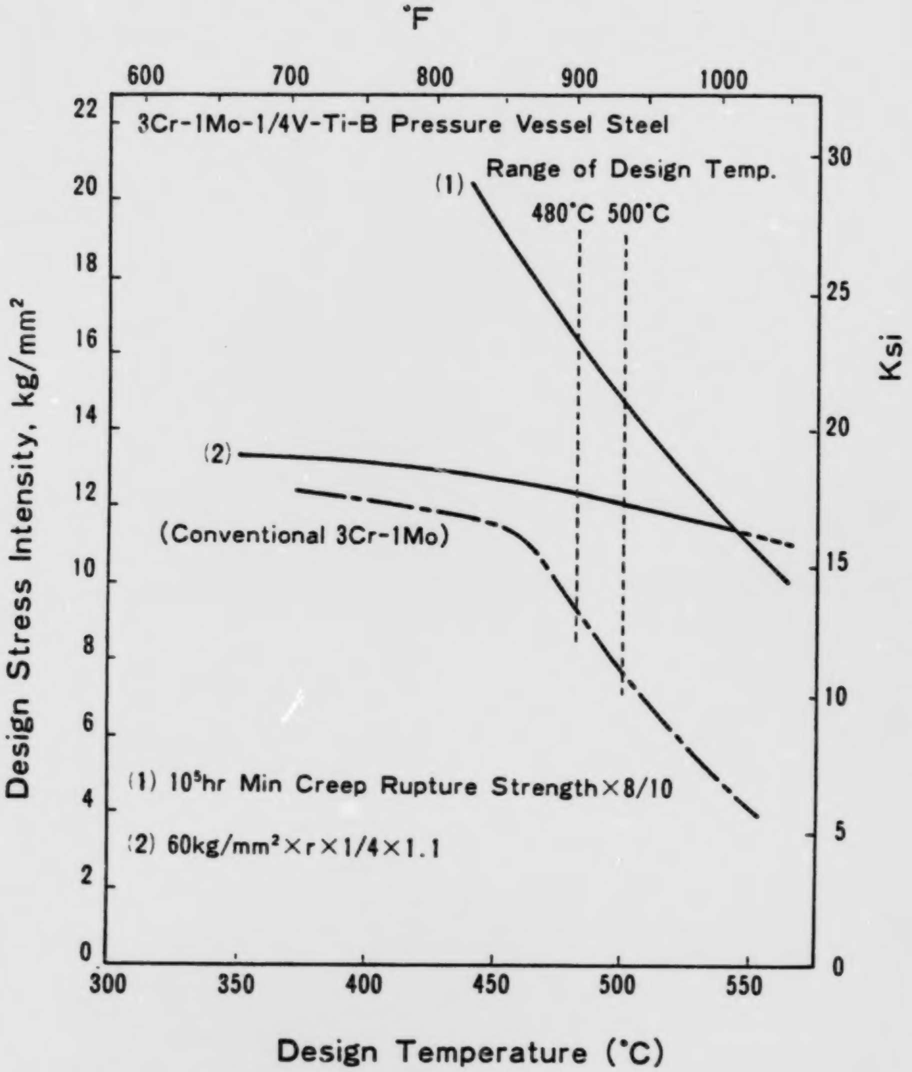

Fig. 6 – Design stress intensity of new alloy in comparison with conventional steel

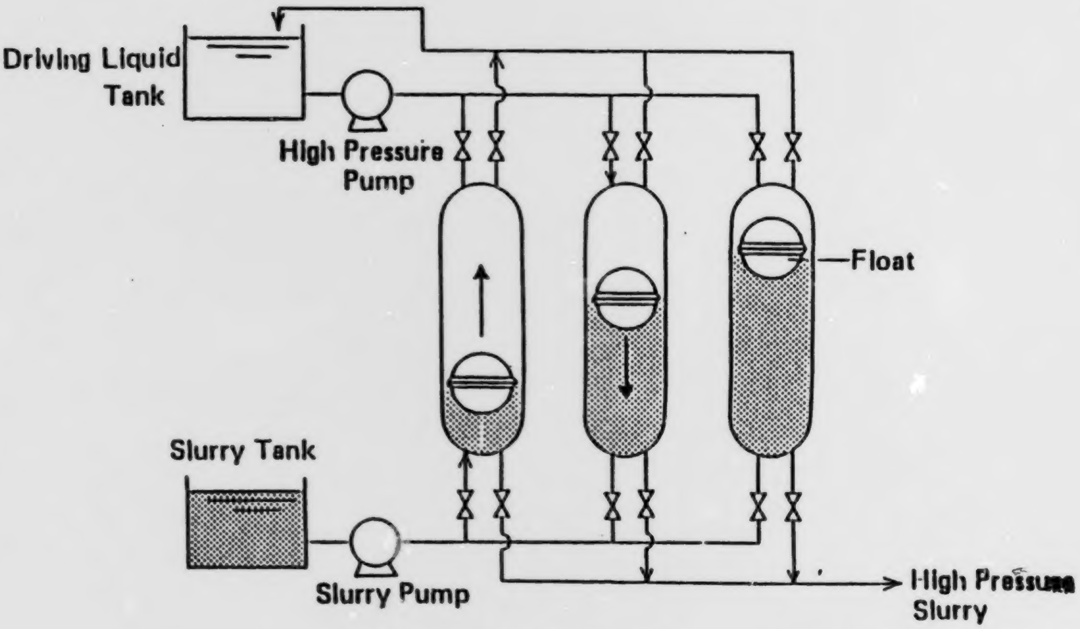
Driving Liquid Tank
High Pressure Pump
Float
Slurry Tank
Slurry Pump
High Pressure Slurry

Fig. 7 – Concept of hydrohoist

SESSION II: PAPER 8

COAL LIQUEFACTION IN THE FEDERAL REPUBLIC OF GERMANY

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ABSTRACT

Upgrading of coal has always been given a prominent position in the German Program for Energy Research and Energy Technologies. In the Federal Republic of Germany, coal is the only primary source of energy which is available for a long time in large quantities from domestic reserves. For this reason, advanced technologies are being developed to obtain cleaner, easier to handle and favourably priced products from coal. These developments are being financed through joint efforts by German industry and public funds. Besides environmentally acceptable methods of generating electricity from coal and coal gasification, the liquefaction of coal is a main topic for research in the field of upgrading coal. Three pilot plants are available for the direct catalytic hydrogenation of coal:

- 200 t/d Pilot Plant Bottrop of Ruhrkohle AG/Veba Oel AG,
- 6 t/d Pilot Plant Saar of Saarbergwerke AG,
- 3 t/d Pilot Plant Lahr of Salzgitter AG/Imhausen Chemie GmbH.

The first two plants have been in operation since 1981; the 3 t/d plant has been ready for operation since September 1984. The technical results gained with these plants are contributing towards necessary data for a decision on the construction of a demonstration plant. As hydrogenation processes are not economical in Germany today, public aid is necessary to realize this large-scale demonstration plant for reasons of supply and industrial policies. In addition to direct hydrogenation, other liquefaction processes are being further developed in R&D projects. Examples of these are the conversion of methanol to gasoline and the pyrolysis of coal.

The paper gives a summary of technologies which are at present being followed in Germany for the liquefaction of coal. It presents the status of the most important individual projects and gives a view of future developments.

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*denotes speaker

PRÉSENTATION 8

LA LIQUÉFACTION DU CHARBON EN RÉPUBLIQUE FÉDÉRALE D'ALLEMAGNE

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RÉSUMÉ

On a toujours accordé beaucoup d'importance à la valorisation du charbon dans le Programme allemand de recherche sur l'énergie et les technologies énergétiques. En République fédérale d'Allemagne, le charbon est la seule source d'énergie primaire disponible à long terme, en quantités importantes, à même des sources intérieures. Pour ce motif, on s'occupe à mettre au point des technologies avancées pour tirer du charbon des produits plus purs, plus faciles à manipuler et moins coûteux. Ces travaux sont financés grâce à des initiatives mixtes prises par l'industrie allemande et les administrations publiques. En plus de méthodes permettant de produire de l'électricité à partir du charbon et de la gazéification du charbon, acceptables dans une perspective environnementale, la liquéfaction du charbon constitue un important sujet de recherche dans le domaine de la valorisation du charbon. On a accès à trois usines pilotes pour procéder à l'hydrogénation catalytique directe du charbon:

- l'usine pilote de 200 t/j de Bottrop, de la Ruhrkohle AG/Veba Oel AG,
- l'usine pilote de 6 t/j Saar, de la Saarbergwerke AG,
- l'usine pilote de 3 t/j Lahr, de la Salzgitter AG/Imhausen Chemie GmbH.

Les deux premières usines fonctionnent depuis 1981, l'usine de 3t/j est en état de fonctionner depuis septembre 1984. Les résultats techniques obtenus contribuent aux données nécessaires à la prise d'une décision concernant la construction d'une usine de démonstration. Comme les procédés d'hydrogénation ne sont pas encore rentables en Allemagne, une aide publique est requise pour construire cette importante usine de démonstration, pour des motifs d'approvisionnement et de politiques industrielles. En plus de l'hydrogénation directe, d'autres procédés de liquéfaction font l'objet de travaux de développement plus poussés, dans la cadre de projets de R-D. A titre d'exemples, retenons la conversion du méthanol en essence et la pyrolyse du charbon.

Cette communication présente un résumé des technologies actuelles utilisées en Allemagne pour liquéfier le charbon; elle precise le statut de la plupart des grands projets et offre une perspective sur les développements éventuels.

**indique le conférencier*

COAL LIQUEFACTION IN THE FEDERAL REPUBLIC OF GERMANY

INTRODUCTION

The development of coal liquefaction in Germany is divided into various phases, which are summarized as follows:

- the origins (1913-1925)
- the first commercial applications (1925-1939)
- the requirements of World War II (1939-1945)
- the conversion of distillation residues until 1963
- the period of cheap oil (1960-1973)
- the oil crisis and the new program for energy research (1974 ...)
- the commercialization of the new technologies.

The period 1913 to 1973 can be described briefly.

The basic work on *coal hydrogenation* carried out by F. Bergius in 1913 showed that the hydrogenizing conversion of coal into liquid products is possible. In the 1920's it was predicted that the future fuel supply of Germany was uncertain. Hence the industrial application of Bergius' idea gained in importance. The chemical industry (I.G. Farben) developed the process of Bergius under the leadership of M. Pier into an industrial process. In 1927 the first hydrogenation plant went into operation in Leuna. The political boundary conditions in the Hitler-era required a self-sufficient supply of gasoline so that, at the end of 1945, 12 hydrogenation plants were in operation producing about 4 mill. t/a liquid fuel (Fig. 1). After the end of the war, three plants (Gelsenberg, Scholven (Photo 1) and Wesseling) were operated in the Federal Republic of Germany (FRG) until 1963 for the hydrogenizing conversion of crude-oil distillation residues. In the period of cheap oil up to 1973 there was no trace of a serious interest in coal hydrogenation.

The development of the *synthesis* of fuels from gases rich in H_2 and CO progressed similarly with respect to time. This synthesis is closely connected with the names F. Fischer and H. Tropsch. Nine plants with a total production of about 0.6 mill. t/a primary products were put in operation before 1945 (Fig. 2). Commercial plants using the Fischer-Tropsch synthesis have been operated in South Africa since 1955.

New energy research programs started in many countries after the oil crisis in 1973. The main aims were to guarantee the supply of energy and to reduce the dependency on imported oil. In the FRG, whose only domestic fuel raw material worth mentioning is coal, great efforts, financially and in terms of personnel involved, were made in order to guarantee a non-polluting and economic utilization of the coal. Coal liquefaction is one of the long-term components of the German Energy Research Program. This is for two reasons. Firstly, this very sophisticated technology requires long periods for development and considerable funds and, secondly, an economic utilization in the FRG is only to be expected in the distant future because of the high (and subsidized) coal prices. However, the technology can be correspondingly applied earlier in countries where coal prices are more favourable.

As already mentioned, there are different methods of obtaining liquid products from coal. In the following sections the development of coal liquefaction will be described from 1974 until today. The reasons for work in the Fischer-Tropsch synthesis only being pursued on a small scale within the Energy Research Program are presented in Section 1. Section 2 describes the conversion of methanol (which can originate from synthesis gas from coal gasification) into gasoline/diesel. The main topic for R&D efforts on coal liquefaction in the FRG is the direct hydrogenation of coal. Section 3 describes the present status of the development. Section 4 presents R&D work on the hydrogenation of heavy crudes, a field which is closely related to coal hydrogenation, as well as work on the possibility of simultaneously converting coal and oil residues. Following this, the pyrolysis of coal will be treated briefly in Section 5. In Section 6 questions of cost-effectiveness and the introduction of coal liquefaction onto the market in Germany and in other countries will be discussed.

COAL LIQUEFACTION BY MEANS OF THE FISCHER-TROPSCH SYNTHESIS

After the Second World War, the Fischer-Tropsch synthesis was operated further to a limited extent by Schering AG in their Bergkamen works. This plant was used primarily to produce fuels, as is also the case for the Sasol I to III plants in South Africa. At the beginning of the sixties the Schering plant was shut down because of pressure from cheap mineral oil on the market.

After the first oil crisis the question of supply with chemical raw materials and chemical basic materials was critically investigated to the same extent as considerations of an energy research program were made. It was recognized that the Fischer-Tropsch synthesis offered more possibility of winning chemical basic materials on the basis of coal than the possibility of contributing to a guaranteed supply of energy in Germany (Fig. 3). This was due to two reasons. For the production of fuels the combination coal gasification Fischer-Tropsch synthesis was being commercially used in South Africa, so that here government support of R&D was scarcely needed any longer. Secondly, because of its notably poorer efficiency, the Fischer-Tropsch synthesis cannot compete with the direct hydrogenation of coal. However, this requires a feed coal that can be hydrogenized (volatiles $> 30\%$ waf, ash content $< 10\%$ waf). In this connection it will be interesting to see which technology is used as a follow-up plant Sasol IV.

R&D tasks on the Fischer-Tropsch synthesis aimed towards guaranteeing the supply of raw materials have as their main objective an increase in the selectivity in order to be able to produce the C_2-C_4 olefins, for example, directly with higher yields.

The most attractive hydrocarbons regarding demand and proceeds would then be obtainable from a coal basis. The development of suitable selective catalysts particularly for this was undertaken by Ruhrchemie AG and several colleges of advanced technology. In close cooperation with technical colleges, in particular with the Berlin University of Technology, Schering AG worked out the *slurry phase* concept. Using this concept the catalysts approached their specific performances, as produced on a laboratory scale, even in continuous operation.

In spite of notable success in the early stages, this work soon reached a phase where one was still too far away from the aim of the development but could practically no longer come any closer to this goal, even in the case of a great variety of research and intensive efforts.

Competition to this was provided by the Mobil-process, which easily satisfied the best expectations that were held for the selective Fischer-Tropsch synthesis.

The circumstances briefly presented here finally led to the fact that no more public money was made available for the development of the Fischer-Tropsch synthesis.

CONVERSION OF METHANOL INTO GASOLINE AND DIESEL OIL

The process chain in the production of gasoline from coal by means of the catalytic conversion of methanol into gasoline is shown in Figure 4. Methanol produced by coal gasification is converted into low-boiling hydrocarbons and water in a *methanol-to-gasoline* (MTG) plant. An alkylation process is added to improve the yield of gasoline. As shown in Figure 4, in this way 39 t gasoline, 3 t LPG and and 2 t methane/ethane are produced from 100 t methanol. On the other hand 56 t water are also produced according to the stoichiometry.

The synthesis of methanol from synthesis gas is a mature process available commercially. Developments in recent years allow reactors with a methanol production of from 2500 to 5000 t/d to be installed; this means up to more than 1.5 mill. t/a. If optimum process conditions are given, the selectivity for methanol is between 95 and 99%, relative to the total amount of carbonaceous products.

In the seventies, catalysts were discovered based on zeolite and these converted methanol selectively into hydrocarbons with low boiling range. The development of catalysts has not yet been completed. Improvements are possible regarding:

- activity and service life
- selectivity to various product groups (aromatics, olefins)
- cheap, commercial processes for the production of catalysts.

As discoverer of this group of catalysts the Mobil Corporation (U.S.A.) still has a lead over competitors, although this is becoming increasingly smaller. In the FRG an industrial consortium (Degussa AG, Ruhrkohle AG, Imhausen Chemie GmbH) is engaged in its own development of catalysts and processes for converting methanol into gasoline. In the same way, catalysts are being developed by modifying zeolites to obtain a highly selective synthesis activity to produce short-chained olefins from methanol (Hoechst AG).

The fixed-bed and fluidized-bed processes are available for technically carrying out the MTG-process. At first, because of its relatively simple technology, the fixed-bed variant was developed by Mobil up to commercial maturity. A corresponding plant is being built in New Zealand.

However, right from the very beginning, it was known that the fluidized bed offered attractive prospects. These can be represented briefly by means of explaining the process flow of both variants (Fig. 5 and Fig. 6). In the fixed-bed process the heat resulting from the methanol conversion is set free in two stages. First methanol is converted to dimethylether with conventional catalysts in the pre-reactor. Here about 20% of the total enthalpy of the reaction is set free. In the following MTG-reactor, which is operated adiabatically, the remaining reaction enthalpy is freed with the conversion of dimethylether into hydrocarbons. Some of the light product gases have to be recycled here to take away the heat and this naturally reduces the partial pressure of the feed stock. This effect can only be compensated for by increasing the process pressure so that the conversion of methanol can take place at 20-30 bar in the fixed bed. The MTG-catalyst, partly deactivated by a coating of coke, must be periodically regenerated by burning off the surface layer. For this reason, several reactors arranged in parallel are necessary for the fixed-bed process in order to guarantee a constant production.

In the case of the fluidized-bed process the conversion of methanol into gasoline takes place in one stage isothermally. The reaction enthalpy is taken away by a cooler from the fluidized bed. As it is not necessary to recycle the gas, the process pressure can be reduced down to less than five bar. The regeneration of the catalyst takes place continuously during the operation. A small part is always being removed from the reactor. Coke deposits are burnt off in the regenerator. The catalyst reactivated in this way is fed back into the reactor.

However, the fluidized-bed variant requires a comparatively more sophisticated technology and abrasion-proof catalysts.

The Union Rheinische Braunkohlen Kraftwerke AG (URBK) is operating a pilot plant for MTG-synthesis based on the fluidized-bed process (Photo 2). As owner of the rights to the process Mobil provides the catalyst and Uhde works out the engineering for the program. A third of the project costs are being provided by the FRG Ministry for Research and Technology (BMFT), a third by the U.S. Department of Energy (DOE) and the remaining third is distributed between the three industrial partners.

The aim of the project is the development and long-term demonstration of a fluidized-bed reactor for MTG-synthesis with all the advantages mentioned, but by minimizing the disadvantages of fluidized-bed technology. All technical process data will be determined for the design and operation of a commercial plant and the operating conditions optimized.

The MTG plant was ready for operation in mid-1982. The test program of the project is divided into the following three phases, the first two having already been completed.

Phase I: (1983)	Operation of the MTG-pilot plant with external catalyst cooler. This concept offers a maximum in-plant flexibility for working out reliable optimum operating conditions and high plant availability.
Phase II: (1984)	Operation with internal catalyst cooler. This concept has cost advantages compared with the Phase I variant, because of the reduced height of the construction and space requirement for the same reactor output. The operating results of Phase I could be confirmed in spite of the reduced flexibility of the internal cooler.
Phase III: (1985)	Operation of the plant to produce lower olefins (*methanol to olefins, MTO*) which can be converted into gasoline and diesel in an *MOGD* process (*Mobil olefins to gasoline and distillate*) which is licensed by Mobil and which is directly connected onto the plant.

Operational results from Phase I and II can be summarized as follows.

The design data were achieved in their entirety and a large number were considerably exceeded. This was particularly true for the plant availability (97%) and the very low catalyst loss. Further characteristic data of the pilot plant are given in Figure 7.

The test with MTG-gasoline (durene contents up to 4%) in a fleet of cars produced no differences in the driving behaviour compared with conventional premium blend gasoline.

The preliminary tests carried out for Phase III (MTO, MOGD) allow the following results from pilot test runs to be expected:

- methanol turnover and total yield of hydrocarbons correspond to the MTG-method of operation
- yields of light olefins relative to the total hydrocarbons between 70 and 80% wt.

The MTO-process will be carried out in the pilot plant with internal catalyst cooling. If the added MOGD-process is adapted for a maximum diesel output, then 1 t methanol gives 0.24 t diesel, 0.13 t gasoline, 0.07 t heating gas and 0.56 t water.

Finally, it must be pointed out that in this project the last stage before commercial introduction onto the market has now been reached.

The German development of catalysts mentioned at the beginning of this paper can be assessed as promising. Therefore, it is expected that the appertaining process development will be taken up on a pilot scale next year.

COAL HYDROGENATION

In the 1920's processes were developed in Germany up to commercial maturity for the production of gasoline and diesel from coal. With the help of these, almost the total demand for fuels in Germany could be covered in the following period up to 1945. The greatest contribution to this was made by coal hydrogenation.

The basis of the conversion of coal into oils (and gaseous hydrocarbons) is the splitting of coal molecules and hydrogenation. The *classical* IG-hydrogenation process developed for this purpose has proved itself technically but no longer meets present requirements.

However, it forms a reliable basis for further development under present technological and economic boundary conditions. More than ten years ago this line of development in the FRG led to the so-called *I.G.-Neu* process or the *modified Bergius-Pier* process. Of all the coal hydrogenation processes developed worldwide, this process has the highest flexibility in the type of feed coal, the effort required for control is considerably less than in the case of competitive processes, and the experiences gained from the classical process can be applied directly.

The basic characteristics of the I.G.-Neu process are shown in the flow-chart in Figure 8. The ground coal is mixed into a slurry with the catalyst and recycled oil distillate and this is brought up to a reaction pressure of about 300 bar by slurry pumps. After the addition of circulating and fresh hydrogen (from pressurized gasification) and the heating-up of the mixture, hydrogenation takes place in several reactors connected in series. The separation of the residue containing solids from the gaseous products follows in the hot-separator. The latter, after passing through a heat-exchanger and cooler, are separated in a stripper. The liquid phase (coal oil) is distilled into the final products and the circulating gas is fed back into the process after being washed. Some of the coal oil is returned into the process as recycle oil. The residue is gasified for the production of fresh hydrogen. A hydrogen deficit can be compensated for by the steam-reforming of the C_1-C_2 gases produced. The slag occurring in the pressurized gasification is removed in the liquid form and, as melted granules, it does not create any difficulties regarding disposal.

The general aim of present development work is the improvement, both technically and economically, of the original classical I.G.-process. This is taking place on three levels:

Modified process

Today distillate which does not contain asphalt is being used as recycle oil, instead of low-temperature oil and centrifuged oil which was used originally. In this way, the reaction pressure can be reduced from 700 to 300 bar without a decline in yields with respect to both space and time. The result is a clear reduction in the specific investments required for the plant.

Application of modern, proved technology known from the conversion of mineral oil

Included here are the better control of large plants within narrower limits, use of improved materials, more accurate dimensioning of apparatus, more effective aggregate to allow an improved heat flow, etc. This leads to an improved thermal efficiency.

Specific new developments for individual components

Coal-slurry compressors, expansion valves and regulating valves, etc. These developments produce a higher flexibility and availability of the plant.

In all the present research projects, all three levels are being worked on simultaneously but with different intensity.

The basic process data of the I.G.-Neu method of operation have been worked out in continuously operated laboratory plants since the early seventies. (Bergbau-Forschung GmbH, Saarbergwerke AG, Rheinbraun AG). It was recognized that for the individual process stages of coal hydrogenation there are still essential technical possibilities for improvement. These will lead both to an increase in the product yield as well as to a reduction in plant costs. The direct step from the laboratory to large-scale demonstration was regarded as too risky. Since 1981 two pilot plants have been operated in the FRG in order to work out reliable data and scale-up factors. These plants are described in the following sections.

200 t/d coal hydrogenation pilot plant of Ruhrkohle AG and Veba Oel AG in Bottrop (Photo 3)

The main aim of the project Coal-oil plant, Bottrop is the demonstration of a high availability of the pilot plant for a coal throughput of 200 t (waf)/d and a yield of 100 t/d liquid products. It will be checked by (long-term) test programs for how much changes in the apparatus and process engineering in partial stages and variations in the reaction parameters (e.g., reactor load, hydrogen partial pressure, reaction temperature) influence the conversion rate of the overall process. Moreover, the effect of different hydrogenating coals and catalysts is being tested. The layout and a few of the results from the Bottrop plant, operated since 1981, are summarized in Figure 9.

In order to exhaust the full potential of the development it is also planned to apply alternative reactor and reaction concepts. The thermal efficiency of the overall plant will increase through the improved use of reaction heat.

The assessment of the effects of coal-oil production on the environment based on measurements of emissions is an important aspect of this work.

Altogether, because of its high throughput capacity this project is being used to determine reliable scale-up factors for the construction and operation of a coal hydrogenation plant of commercial size (modules with a throughput capacity of about 2500 t coal/d). Work carried out here is essentially concerned with apparatus and only serves in a limited way for process modification.

The companies responsible for the Bottrop-plant have been actively involved in the U.S.A. developments for coal hydrogenation. The experiences from the H-coal, Exxon-Donor-Solvent and Solvent-Refined-Coal-II projects contribute to the database for commercialization of coal hydrogenation.

6 t/d coal hydrogenation plant of GfK (Gesellschaft fur Kohleverflüssigung mbH, 100% subsidiary of Saarbergwerke AG) in Fürstenhausen/Saarland. (Photo 4).

This plant was built with the aim of developing and testing modified process concepts for improving the I.G.-Neu process. In specifying the plant capacity it was appreciated that for cost reasons the plant capacity should be designed as small as possible but with regard to scaling-up it should be designed as large as necessary.

In the period between September 1981 and December 1983, the plant was tested and optimized regarding apparatus and process technology. Besides maximum yield of coal oil, the most important parameters for optimization were long-term stability, controllability and prevention of coking.

The introduction of an intermediate separator, for the direct recycling of hot heavy fractions under process pressure as diluent to the pre-heater, was tested. In this way, about a third of the total recycle oil can be circulated internally. This considerably reduces the load on the pre-heater and distillation.

The vacuum flash distillation of the expanded hot residue (ca. 400°C) from the hot-separator has shown itself to be a problem-free process stage of high availability. The remaining oil-content (boiling temperature below 475°C) of the residue granules can be reduced to 5% for absolute pressures of less than 60 bar. The content of solids in the residue lies between 38 and 50% wt (mineral components of coal, catalysts and remaining unconverted coal).

Altogether the components tested up to now in the pilot plant of the Saarberg-GfK-concept could be confirmed regarding their function and availability.

Figure 10 shows design data and results from the operation of the Saarberg plant.

In the following operating phase new process stages will be tested. These will include:

- Improved energy recovery from the hydrogenation process for directly heating the coal slurry with the objective of dispensing with the problematic heat exchangers. One advantage of this process variant is that gases such as carbon dioxide, water and methane, released when heating the coal, are removed before they can enter the reactor part. Through this preliminary degasification of the coal, a reduction in the overall pressure is possible for the same H_2-partial pressure.
- Higher content of solids in the feed coal slurry up to 70%. Up to now the coal slurry entered the high-pressure system with a solid-content of about 40%.
- Coking of hydrogenation residue to maximize the yield of coal oil.
- Carrying out the slurry-phase hydrogenation in two stages to increase the hydrogen partial pressure for the same overall pressure in the reactors.

In the operating and test concept of the 6 t/d pilot plant presented here, it is intended to test a maximum number of process engineering and basically different innovations in order to bring coal hydrogenation based on the I.G.-Neu process as far as possible towards cost-effectiveness using technical means.

The further conversion of the coal oil into gasoline, diesel, jet fuel and heating oil of the correct specifications, is an important aspect that is being worked on in both of the projects mentioned on the Ruhr and Saar. For commercial application the refining of coal oil (gas-phase hydrogenation) will be directly coupled to coal hydrogenation (liquid-phase hydrogenation). Within the framework of the project at Bottrop, oil from coal is being further converted in the refinery facilities at Scholven, belonging to Veba Oel AG, to give qualities of current specifications. In the pilot plant at Fürstenhausen a catalytic hydrogen-refining (fixed bed) unit was integrated into the pressurized chamber of the liquid phase. The economic assessment of such a concept has not yet been completed.

Results obtained from both pilot plants can be demonstrated by the figures for thermal efficiency. In the classical I.G.-process this was about 40%. Based on results from the pilot plants, today more than 55% is expected for commercial plants.

A new reactor concept for hydrogenation will be tested in a third pilot plant whose construction was completed in September 1984:

3 t/d coal oil plant Lahr, of Salzgitter AG/Imhausen Chemie GmbH (Photo 5).

In all the coal hydrogenation plants up to now, the reactors have the characteristic of agitator vessels. This project is to investigate for the first time a slurry phase reactor which has the character of a reaction tube. Lying down, this reaction tube can be divided up into five sections and has a length-to-diameter ratio of about 10,000:1. The advantages specific to the reaction of the tube-reactor principle and modifications to the method of operation – in particular higher temperature (460-510°C) and pressure (700-1500 bar) – mean that improvements are to be expected in the throughput, yield and selectivity, and hence in the profitability and effect on the environment of direct coal hydrogenation using this new process concept. These improvements considerably overcompensate for the extra costs for higher process pressure.

HEAVY CRUDE HYDROGENATION

The refining of heavy crude and residue is gaining in importance for energy supply. The upgrading of residues from refineries contributes towards the continuing refining of normal mineral oil to fuels, light heating oil and chemical raw materials.

The proved heavy crude reserves with deposits in Venezuela, Canada and the U.S.A. are of the same order of magnitude as the reserves of conventional crude oil. In the long term it will therefore be necessary to adapt existing refining capacity for upgrading heavier oils.

The development work on upgrading heavy crudes and residues was considerably affected by the cooperation since 1978 between German industrial companies and Venezuelan oil companies that takes place under the auspices of a governmental agreement between the Federal Republic of Germany and the Republic of Venezuela. Here the hydrogenation technology also developed for coal hydrogenation, and which is characterized by flexibility and high conversion properties, can be applied advantageously.

Based on investigations carried out up to now, *the Veba-Combi-Cracking (VCC)* process offers the best prospects for upgrading bituminous heavy crude and residues to light and middle distillates. As can be deduced from Figure 11, the VCC-process is very similar to the I.G.-process for coal hydrogenation. Only the special feedstock preparation and recycle solvent are missing. The VCC-process goes back to the Bergius-Pier process developed for the hydrogenation of hard coal. After the Second World War, following minor modification, Veba Oel Ag adapted the existing coal plants for the conversion of residues (Photo 1). In this way, the process was further developed through the direct combination of the slurry and gas phase to the *Scholvener Kombi Kammer*, which is the direct forerunner to the VCC-process. In 1978 the development of the VCC-process was taken up again on this technical basis. At Veba Oel AG, basic investigations were carried out for a large palette of different oils, first of all in one technical-scale plant and then in a second.

A 24 t/d pilot plant began operating in 1983 in cooperation with Lurgi GmbH (Photo 6). In this plant the combination of the liquid and gas phase hydrogenation is being tested. It is being used to determine and confirm scale-up factors for the construction and operation of a commercial plant (capacity 2500 t/d feed material per train). The conversion rates of feedstock to distillate realized with this process up to now are more than 95%.

A preliminary study on the planning and process engineering design of a large plant for the hydrogenation of residues and heavy crude for a German location is running parallel to the operation of the pilot plant.

The development is accompanied by university projects in order to develop other suitable processes for upgrading heavy crudes and bitumina and to improve the existing process. In this connection it was found that mixtures of lignite and mineral oil residues are in principle suitable for a joint hydrogenation based on the I.G.-Neu concept. This idea is being considered in more depth by Rheinbraun AG.

Contrary to the negative experiences in the period before 1945, a joint hydrogenation of hard coal and mineral-oil-based hydrogenation residues is also possible. This is implied by test results from the 6 t/d pilot plant in Fürstenhausen.

COAL LIQUEFACTION BY PYROLYSIS

In addition to synthesis and coal hydrogenation, pyrolysis can be applied as the third method of coal liquefaction. The simpler process technology must be set against a reduced yield in liquid products. Within the framework of a project of the International Energy Agency (IEA), basic experiments on pressurized pyrolysis and pyrolysis in a hydrogen atmosphere have been carried out since 1978 by Bergbau-Forschung GmbH (Germany, as operating agent), the Lund Institute of Technology (Sweden) and the Coal Research Establishment of the National Coal Board (England). A comprehensive report on experiments in the milligram-to-gram range was given at the CANMET meeting in 1982. The commercial prospects for pyrolysis are being estimated as favourable by the project partners – but with the reservation that the results are only based on laboratory tests. After the completion of detailed engineering work on a pyrolysis plant on the kg/h scale, such a plant will now be built and go into operation at about the beginning of 1986. The main part of the plant will consist of an entrained flow reactor, about 3 m long, connected to a coke separator and condensate precipitator. The tar products can be directly cracked by heating in the connected installation. The maximum pressure possible is 200 bar.

An integration of Canadian work into the IEA-project was unfortunately not possible.

COST-EFFECTIVENESS OF COAL LIQUEFACTION AND ITS INTRODUCTION ONTO THE MARKET

An exact presentation of the cost-effectiveness and introduction onto the market of coal liquefaction is impossible because of the many suppositions which have to be made on the future development of energy demand and prices. However, based on the two process chains, MTG and hydrogenation, a few trends will be shown which cover the difficulties of an assessment.

First of all, the process chain *coal-synthesis gas-methanol-gasoline* will be considered. The up-grading of coal (or of natural gas and bunker oil) into synthesis gas and the methanol synthesis can be regarded as commercially available technologies. The development of the upgrading of methanol into gasoline/diesel in a catalytic fluidized bed will be completed at the end of 1985 after the 21 t/d demonstration plant has been operated for some years. Commercial projects with fixed-bed catalysts will have been realized by then (New Zealand). Here it is relatively easy to assess the improved technique regarding its future application possibilities. An estimation of the product costs for MTG-gasoline has been undertaken (Fig. 12) and it is not to be expected that the technological boundary conditions will change considerably before a decision for, or against, commercial plants can be taken. As shown in the figure, the price of gasoline for a given price for methanol depends on the technology chosen. The changeover from fixed-bed to fluidized-bed catalysts reduces the conversion costs and hence the gasoline costs. The price of methanol on the German market is 450 DM/t at present and this gives costs for gasoline of between 1300 DM/t (fluidized-bed catalyst) and 1450 DM/t (fixed-bed catalyst). However, the market price for gasoline is 800 DM/t. It can be asked, how high can the price of methanol be, in order to produce gasoline for 800 DM/t? Furthermore, from the figure it can be deduced how high the price of the feed materials applied in the chain *synthesis gas-methanol-gasoline* can be assumed. Compared with today's prices for natural gas, bunker oil and hard coal in Germany, the resulting prices are considerably lower. Here it is clear that it is not the technical development which considerably alters the economic consideration, but that the ups and downs of the prognoses of prices of raw materials determine the economic assessment. At present, this technology is only applicable for extremely favourable deposits of natural gas, or in the case when the state subsidizes the technology for reasons of energy policy and structural policy. In future, the process chain *coal-methanol-gasoline* can gain in importance in the case of rising prices for crude oil and natural gas.

The plant capacity given in the figure is 10^6 t MeOH/a. This corresponds to about 1.4 10^6 t coal/a or to 0.4 10^6 t gasoline/a as product in the process chain *coal-methanol-gasoline*. In the case of plants using this technology, for the capacity field given, the cost digression is already completely effective, meaning relatively small plants can be built in modular form with correspondingly reduced total investment costs.

If one considers the economically optimum size for a coal hydrogenation plant, then it becomes clear that the cost digression only becomes completely effective at 2 to 3 mill. t product/a. This will be a disadvantage in the introduction of this technology.

A glance at the time-schedule for the development of coal hydrogenation plants (Fig. 13) shows that the earliest possible operation of a commercial plant will not be before the end of the century. To achieve this, the construction and operation of a demonstration plant with a capacity of 1 to 2 mill. t coal/a is necessary. At the moment in Germany intensive thoughts are being given to such a plant. Technology, location, capacity, product spectrum, environmental aspects, connection to the existing infrastructure and costs are the main aspects in the engineering studies. Equally important are questions of financing and cost minimization while keeping as far as possible to the demonstration character of the plant and the organizational aspects of such a large project. These factors are being discussed among the industrial firms involved and the responsible Federal and State Ministries. It is clear to all those concerned that a demonstration plant in Germany cannot be operated economically, so that governmental support is necessary. On the one hand this is because of the high prices for German coal and on the other hand because of the stable oil price level. Only dramatic oil price rises in the next ten years (nobody is hoping that these will occur), could mean that the demonstration plant would manage on relatively low grants.

A survey on the engineering work for demonstration and commercial concepts of coal hydrogenation is given in Figure 14.

From technical and economic points of view, a commercial heavy crude hydrogenation plant could be built concurrently to the demonstration plant for coal hydrogenation as planned in the time-schedule. For this reason, an interesting alternative to the demonstration of coal hydrogenation is at present being checked within an engineering study. This is the possibility of testing a train of such a crude-oil hydrogenation plant for a limited period of time for coal operation. Such a procedure would save both time and costs. However, it has still to be shown whether the aims of a demonstration plant could really be achieved in this way.

The prospects for the commercial application of hydrogenation technology are even more difficult to estimate than the costs for the demonstration project. Who can accurately predict today how the price level for the different sources of energy will develop in the period up to 2000 and then further over the whole lifetime of the plants? Who can predict today whether the technical development significantly influences the investment and operating costs? A glance at the cost structure for hydrogenation products shows the following distribution for a large commercial plant in the FRG, status 1983:

- 40% coal costs (hard coal)
- 25% operating costs
- 35% capital costs.

This picture changes if one can replace the expensive German hard coal with cheaper lignite or imported coal, or if one changes the plant location to where there is cheaper coal available.

Naturally the term *status 1983* is hardly realistic. As already mentioned, commercial plants will not be going into operation until after 2000. For this reason, dynamic economic calculations will have to be carried out to decide the values given to inflation rates for investments, operating costs, feed coal and products. Boundary conditions for financing the investment costs must be given for a period which lies far ahead in the future. Without going into detail of the values used and calculations carried out, the main influences on the profitability of commercial plants are given in the following parameters:

- Values of the different rate of inflation between coal and product. A difference of more than 2% (for instance 4%/a for coal and more than 6% for product) can make the hydrogenation technology using expensive German coal economic.
- Location and hence the coal quality, coal costs, infrastructure, product spectrum, etc.
- Plant availability.
- Investment costs.

Only the last two points can be influenced by technical development, and it is exactly this effect which the German R&D program hopes to achieve.

FINAL COMMENT

The development of coal upgrading technologies was taken up again in Germany mainly out of fear that supply bottlenecks could arise with mineral oil and gas. In the period up to today this has never been the case. However, we have only a period of about 10 years out of a total of the 25-30 year development period behind us. It was not, and is still not, to be expected that the now coal-liquefaction technologies will offer help quickly in short-term supply crises caused politically. With regard to energy and supply policy in the Federal Republic, this motto is still valid: *We will not be able to dispense with our coal for energy supply for a long time.* Hence it is reasonable to continue to strive towards the objectives, formulated under the influence of the energy crisis, regarding the upgrading of coal.

Coal technologies developed and still to be developed could be applicable earlier for other countries than is the case for Germany. Advanced coal technologies such as hydrogenation can compete against oil imports, which are always becoming scarcer and more expensive, in particular in countries where coal can be mined cheaply. Whether German industry can succeed in such markets depends essentially on whether the high status of technology obtained can be maintained.

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FIGURES

Start of operation	Plant location	Feed material	Pressure (bar) Liquid Phase	Pressure (bar) Gas phase	Product Capacity t/a
1927	Leuna	lignite, tar	200	200	650,000
1936	Böhlen	lignite tar	300	300	250,000
1936	Magdeburg	lignite tar	300	300	220,000
1936	Scholven	hard coal	300	300	280,000
1937	Welheim	pitch	700	700	130,000
1939	Gelsenberg	hard coal	700	300	400,000
1939	Zeitz	lignite tar	300	300	280,000
1940	Lutzkendorf	tar, oil	500	500	50,000
1940	Politz	hard coal, oil	700	300	700,000
1941	Wesseling	lignite	700	300	250,000
1942	Brux	lignite tar	300	300	600,000
1943	Blechhammer	hard coal, tar	700	300	420,000
					4,230,000

Fig. 1 – German hydrogenation plants 1943/44

Plant location	Originally planned product capacity (t/a)
Bergkamen	75,000
Castrop-Rauxel	50,000
Dortmund	60,000
Wanne-Eickel	60,000
Moers	75,000
Holten	70,000
Odertal (Oberschles.)	60,000
Schwarzheide	210,000
Lutzkendorf	80,000
	740,000
(achieved capacity	570,000)

Fig. 2 – German Fischer-Tropsch Plants 1943/44

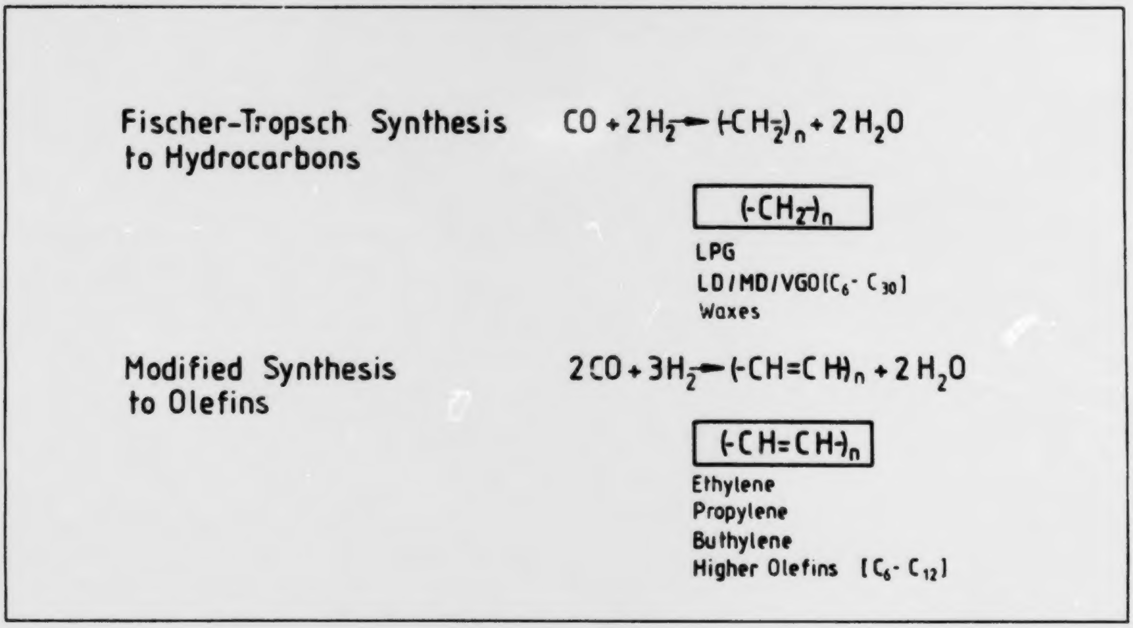
Fischer-Tropsch Synthesis to Hydrocarbons
$CO + 2H_2 \rightarrow (-CH_2-)_n + 2H_2O$
$(-CH_2-)_n$
LPG
LD/MD/VGO $[C_6 - C_{30}]$
Waxes
Modified Synthesis to Olefins
$2CO + 3H_2 \rightarrow (-CH=CH-)_n + 2H_2O$
$(-CH=CH-)_n$
Ethylene
Propylene
Buthylene
Higher Olefins $[C_6 - C_{12}]$

Fig. 3 – Fischer-Tropsch synthesis

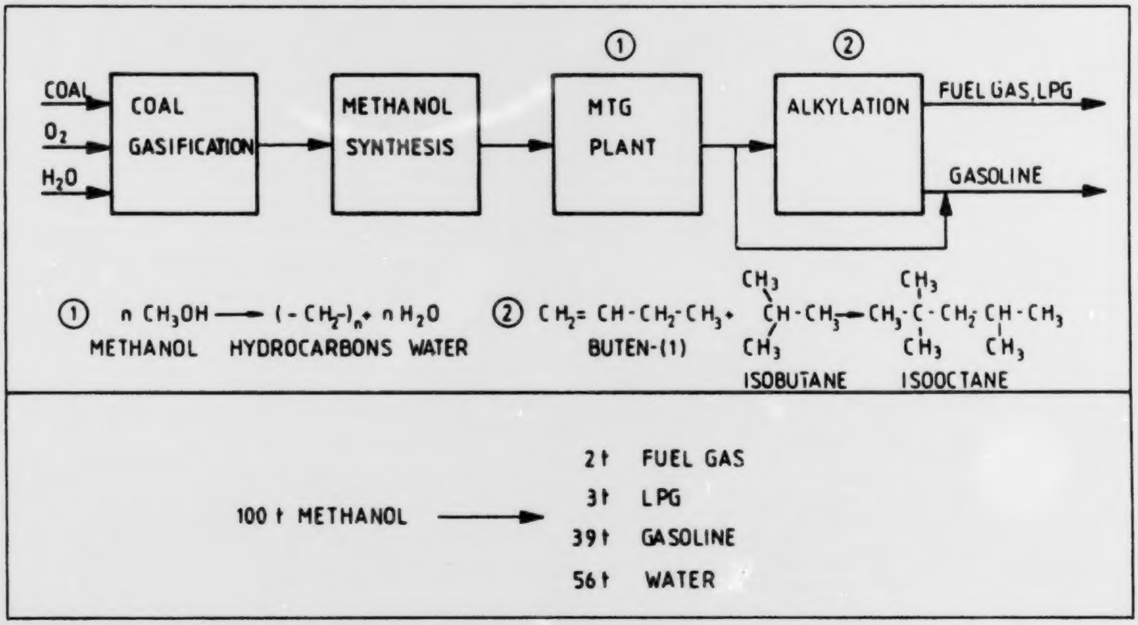
①
②
COAL
O_2
H_2O
COAL GASIFICATION
METHANOL SYNTHESIS
MTG PLANT
ALKYLATION
FUEL GAS, LPG
GASOLINE
① $n\,CH_3OH \rightarrow (-CH_2-)_n + n\,H_2O$
METHANOL HYDROCARBONS WATER
② $CH_2=CH-CH_2-CH_3 + CH(CH_3)_2-CH_3 \rightarrow CH_3-C(CH_3)_2-CH_2-CH(CH_3)-CH_3$
BUTEN-(1)
ISOBUTANE
ISOOCTANE
100 t METHANOL
2 t FUEL GAS
3 t LPG
39 t GASOLINE
56 t WATER

Fig. 4 – Coal liquefaction via MTG process

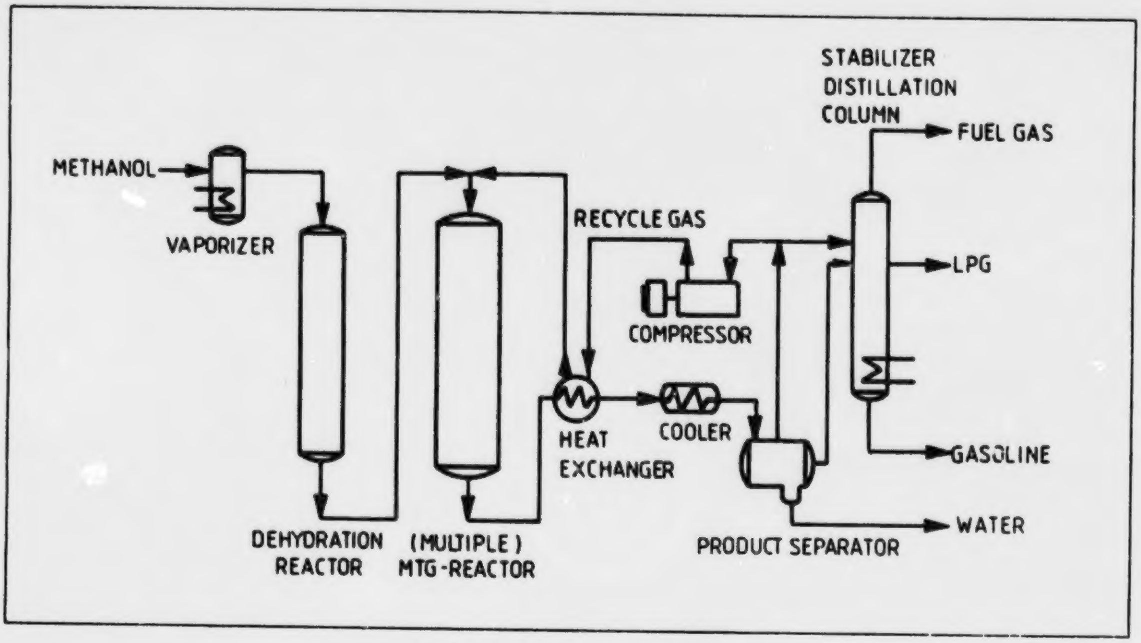
STABILIZER
DISTILLATION
COLUMN
FUEL GAS
METHANOL
VAPORIZER
RECYCLE GAS
LPG
COMPRESSOR
HEAT
EXCHANGER
COOLER
GASOLINE
WATER
DEHYDRATION
REACTOR
(MULTIPLE)
MTG-REACTOR
PRODUCT SEPARATOR

Fig. 5 – MTG – fixed-bed process

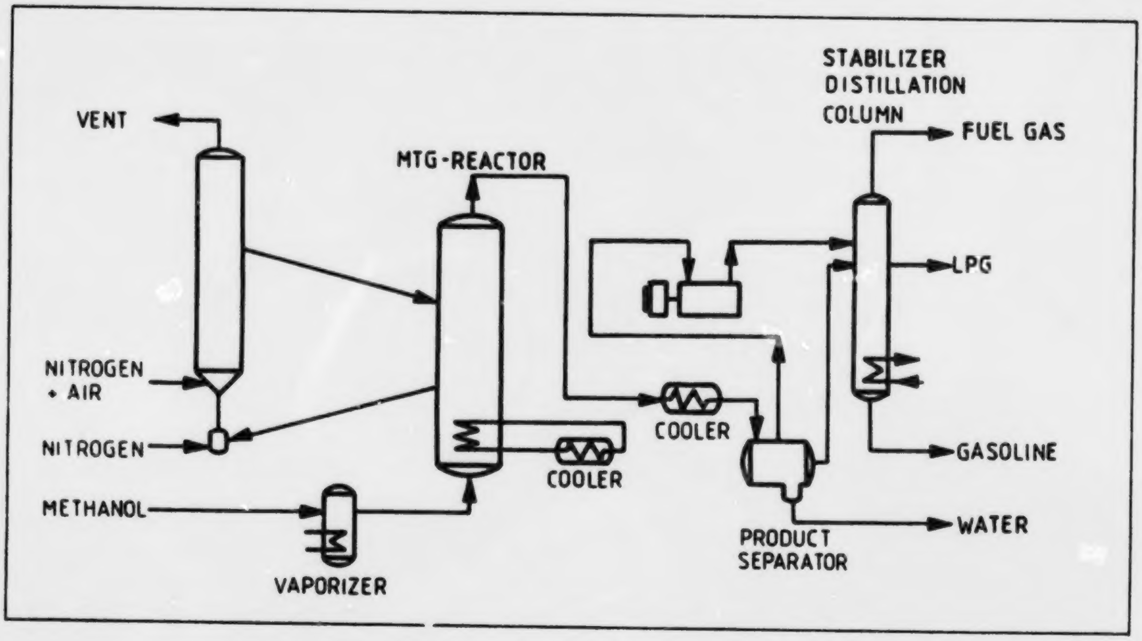
STABILIZER
DISTILLATION
COLUMN
FUEL GAS
VENT
MTG-REACTOR
LPG
NITROGEN
+ AIR
NITROGEN
COOLER
COOLER
GASOLINE
METHANOL
WATER
PRODUCT
SEPARATOR
VAPORIZER

Fig. 6 – MTG – fluidized-bed process (external catalyst cooler)

Reactor pressure	2.7 - 4.5	bar
Reactor temperature	380 - 430	°C
Weight hourly space velocity (kg MeOH/kg catalyst · h)	0,5 - 1,5	h^{-1}
MeOH feed	135 - 200 (700 - 1050	bpd kg/h)
Conversion rate	> 99,99	%
Max. Gasoline yield (incl. alkylates)	90,00	%
Plant availability	> 95,00	%
Catalyst losses	very low	
Gasoline quality	according to DIN-standard	
RON/MON (clear)	95,2/85,4	
RON/MON (0.15 TEL/l)	98,6/88.7	

Fig. 7 – Fluidized-bed MTG pilot plant – test results

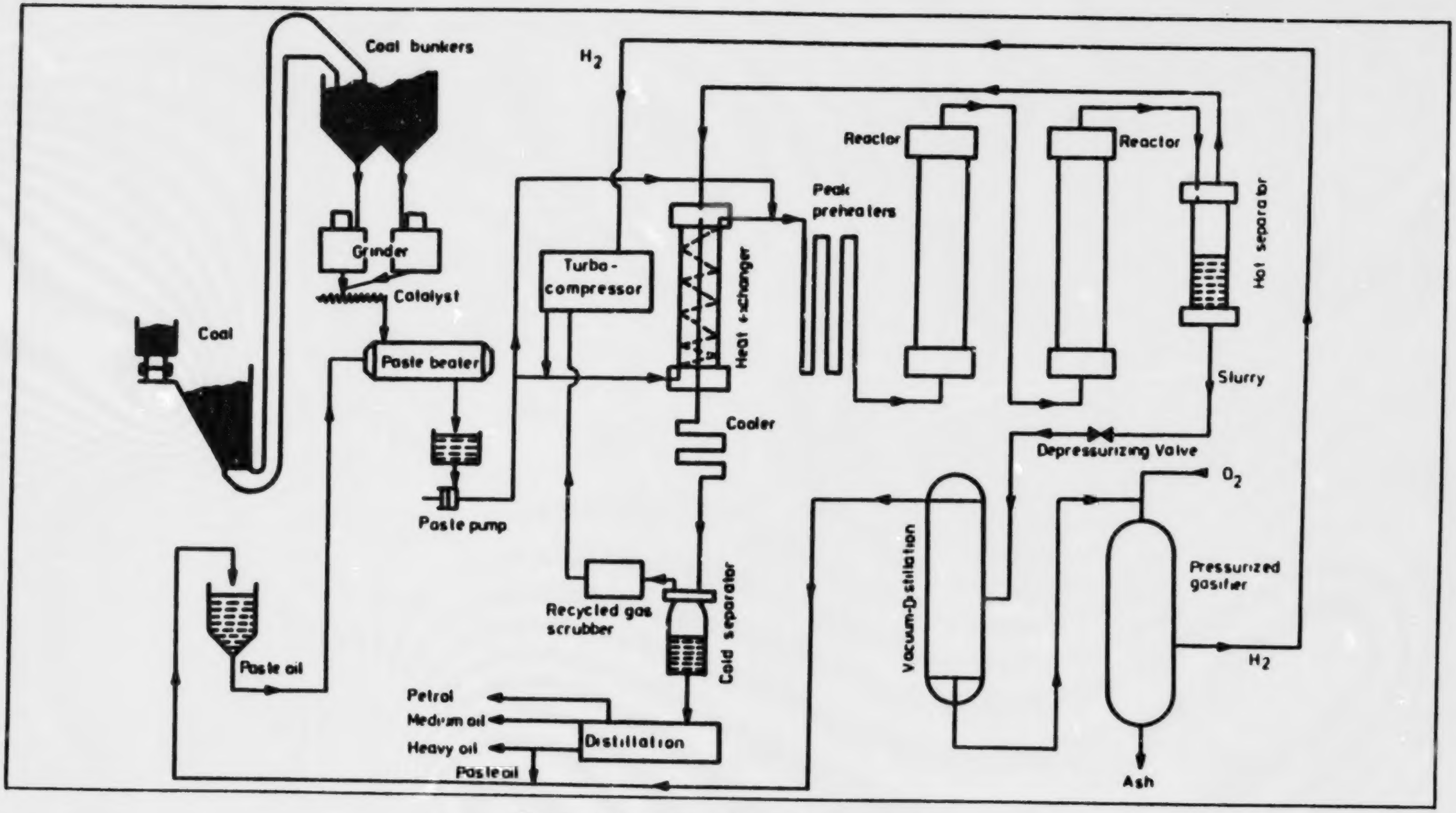
Coal bunkers
H_2
Coal
Grinder
Catalyst
Paste beater
Paste pump
Paste oil
Turbo-compressor
Heat exchanger
Peak preheaters
Reactor
Reactor
Hot separator
Slurry
Depressurizing Valve
O_2
Cooler
Recycled gas scrubber
Cold separator
Vacuum-Distillation
Pressurized gasifier
H_2
Petrol
Medium oil
Heavy oil
Paste oil
Distillation
Ash

Fig. 8 – I.G.-Neu coal hydrogenation process

Process	IG-neu
Coal Capacity	200 t (waf)/d
Construction	1979 - 1981
Operation	1981 -(1986)
Coal Feed	Westerholt, Prosper (Ruhr) Illinois (USA)
Pressure	300 bar
Temperature	475-490°C
Catalyst	Bayer - Masse
Spec. coal througnp.	0.4-0.5 t(waf)/m^3 h
Operation time*	16,000 h
Operation time with coal*	12,300 h
Longest run*	3,100 h

Input coal	Prosper
ash (wf)	5.9 % wt.
volatile matter (waf)	36.8 % wt.
Yield (waf)	
gases	23.0 % wt.
naphtha (-200°C)	15.0 % wt
middle dist. (-325°C)	35.0 % wt.
oil in residues	7.0 % wt.

*Sept. 1984

Fig. 9 – Design data and results of the 200 t/d pilot plant or coal hydrogenation at Bottrop (Ruhr)

Process	IG-neu
Coal Capacity	6 t (waf)/d
Construction	1979 - 1981
Operation	1981 -(1986)
Coal Feed	Ensdorf (Saar)
Pressure	300 bar
Temperature	460-483°C
Catalyst	Bayer - Masse
Spec. coal throughp.	0.4-0.7 t(waf)/m^3h
Operation time*	7,200 h

Input coal	Ensdorf
ash (wf)	6.2 % wt.
volatile matter (waf)	37.2 % wt.
Yield (waf)	
gases	15.9 % wt.
naphtha (-200°C)	12.8 % wt.
middle dist. (-325°C)	27.7 % wt.
heavy dist.	16.5 % wt.
oil in residues	>5.0 % wt.

*Jan. 1984

Fig. 10 – Design data and results of the 6 t/d pilot plant for coal hydrogenation at Furstenhausen (Saar)

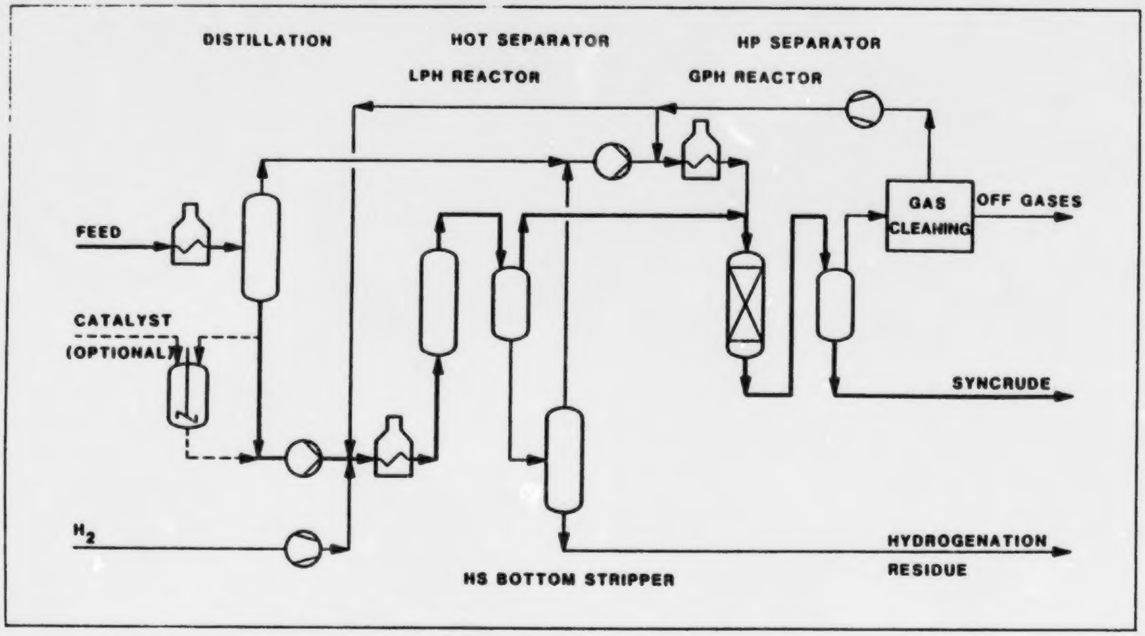
DISTILLATION
HOT SEPARATOR
HP SEPARATOR
LPH REACTOR
GPH REACTOR
FEED
GAS CLEANING
OFF GASES
CATALYST (OPTIONAL)
SYNCRUDE
H_2
HYDROGENATION RESIDUE
HS BOTTOM STRIPPER

Fig. 11 – Veba-Combi-cracking (VCC) – simplified flow scheme

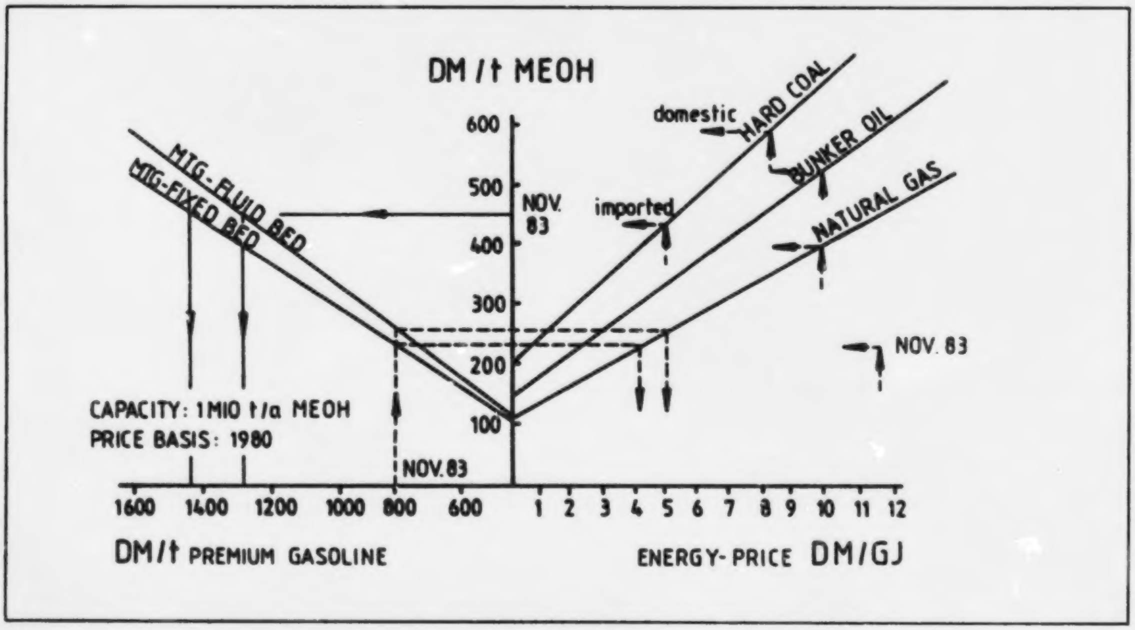

Fig. 12 – Production costs for MTG – gasoline

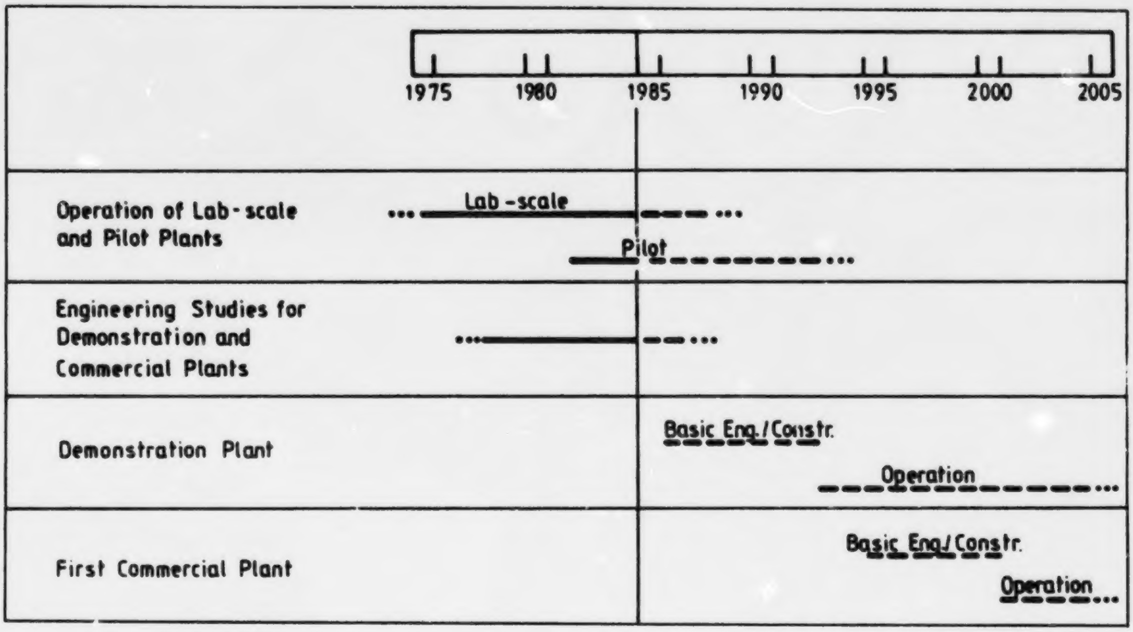

Fig. 13 – Time schedule for hydrogenation of coal – earliest possible dates

Industrial companies	Process	Capacity (coal or oil, t/d)	Feed	Time frame
Imhausen (Coord.)	Fischer-Tropsch + IG-neu	Commercial size	German coal	1978 - 1979
Imhausen (Coord.)	Fischer-Tropsch + IG-neu	Commercial size	Australian coal	1979 - 1981
Ruhrkohle	IG-neu	5.000	bit. coal	1980 - 1981
Veba	IG-neu	2.000	bit. coal/ oil resid.	1980 - 1981
GfK/Saarberg	IG-neu	5.000	bit. coal	1980 - 1982
Rheinbraun	IG-neu	4.000	lignite ($10-12\%H_2O$)	Pre-study 1983
Gulf/RAG/Mitsui	SRC-II	6.000	bit. coal	1980 - 1981
Veba, Lurgi, KWU, Steinmüller/PdVSA + affiliates	VCC	16.000	heavy oil	1979 - ....
Veba/Lurgi	VCC	5.000 2500/2500	oil resid. oil r./coal	1982 - ....
Ruhrkohle/Veba	IG-neu	2.500	bit. coal	1983 - ....
GfK/Saarberg	IG-neu	2500/2500	coal/oil r.	1983 - ....
Imhausen (Coord.)	IG-neu	18.000	bit. coal	1983 - 1984

Fig. 14 – Studies for demonstration and commercial projects for hydrogenation of coal and oil (only studies with governmental support)

PHOTOS

Photo 1 – Liquid phase hydrogenation plant Scholven/Horst (hard coal until 1945, various vacuum residues 1952-1964)
Source: VEBA OEL AG

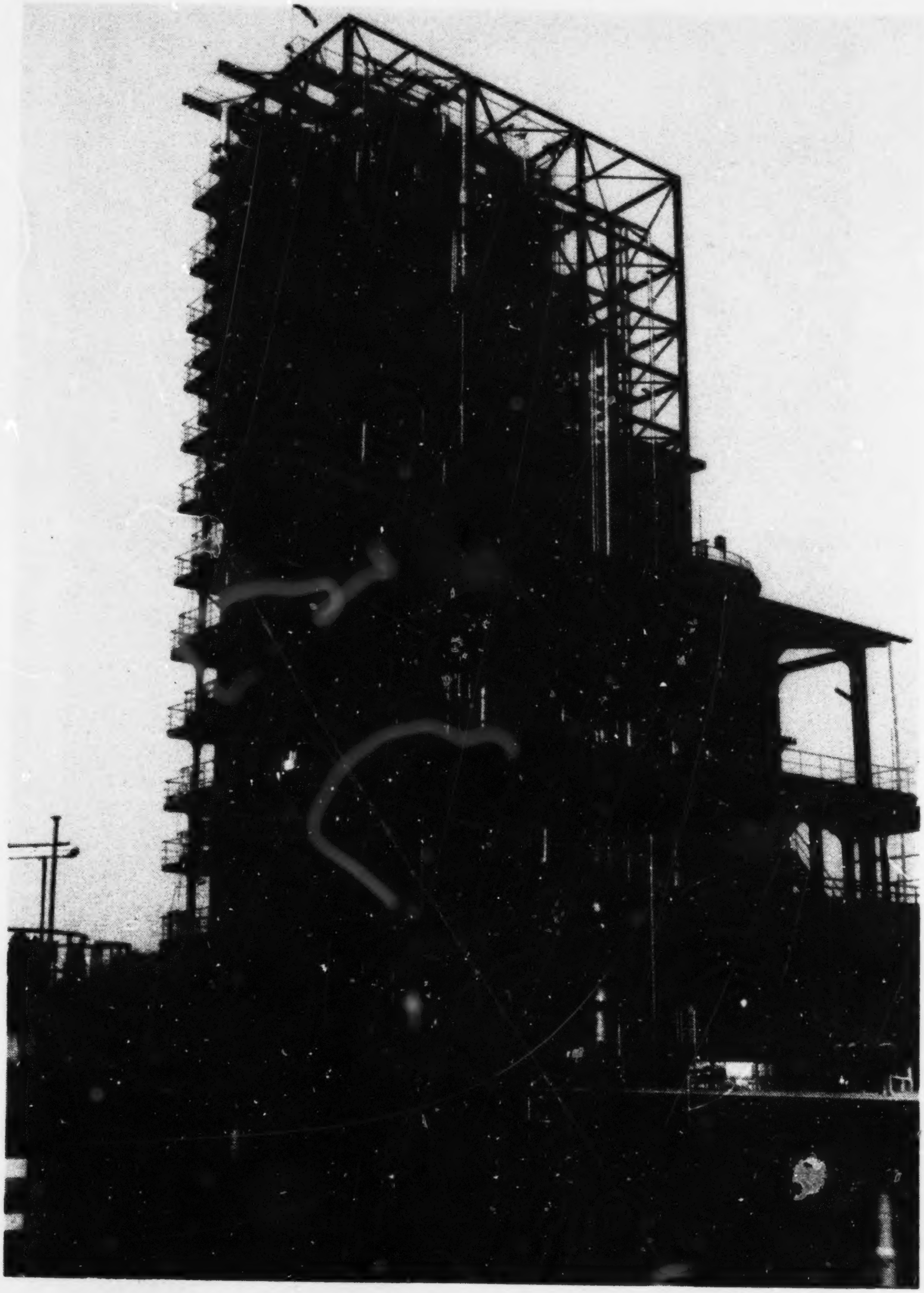

Photo 2 – MTG pilot plant (methanol to gasoline)
Source: URBK, Wesseling

Photo 3 – The 200 t/d pilot plant for coal hydrogenation at Bottrop
Source: Ruhrkohle AG/VEBA OEL AG

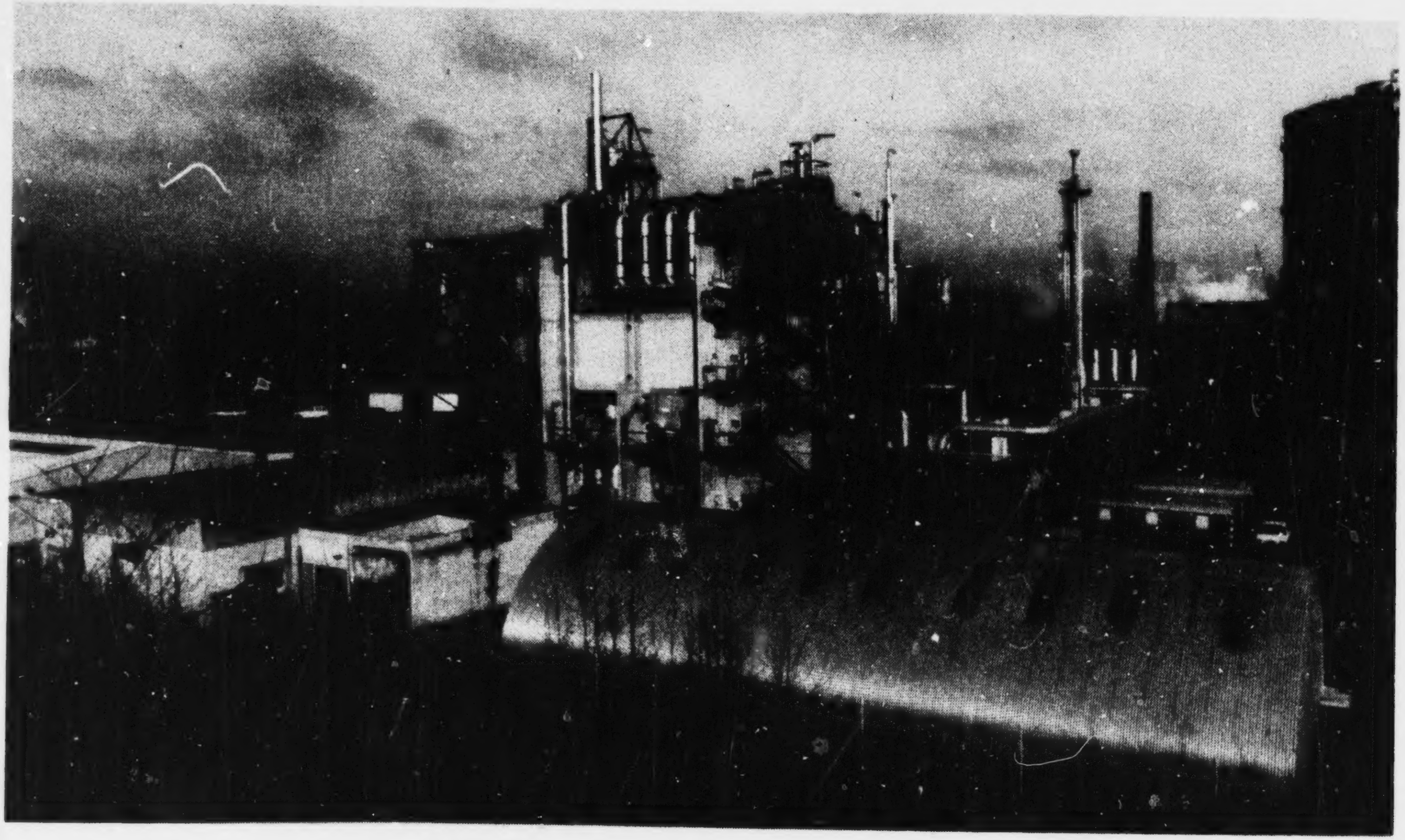

Photo 4 – The 6 t/d pilot plant for coal hydrogenation at Furstenhausen (SAAR)
Source: Gesellschaft fur Kohleverflussigung mbH

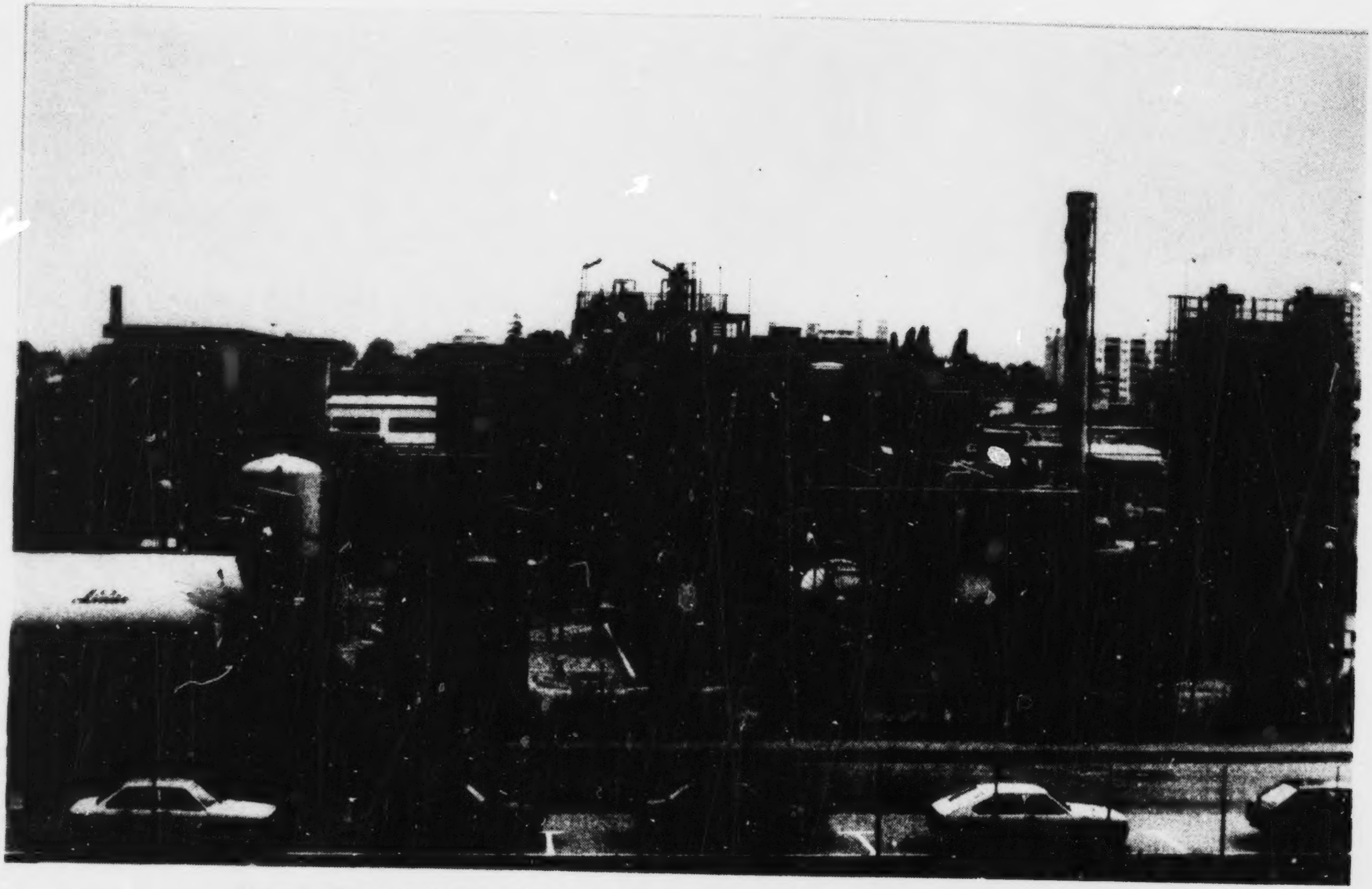

Photo 5 – The 3 t/d pilot plant for coal hydrogenation of Lahr (tubular reactor concept)
Source: Salzgitter AG/Imhausen Chemie GmbH

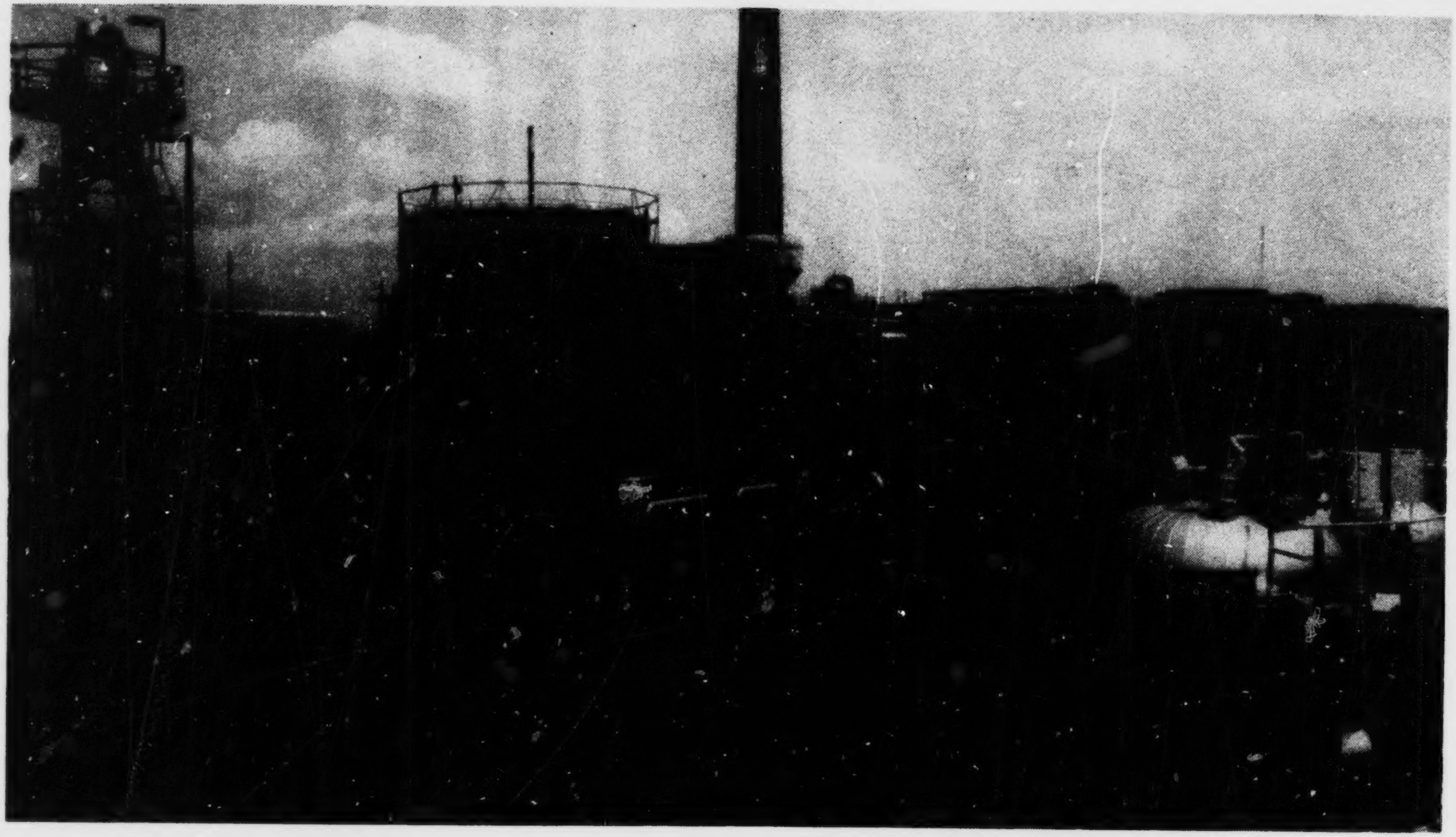

Photo 6 – The 24 t/d pilot plant for hydrogenation of heavy oils and distillation residues at Gelsenkirchen
Source: VEBA OEL AG

SESSION II: PAPER 9

COAL HYDROGEN EFFECTS ON PYROLYSIS AND LIQUEFACTION CONVERSION

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ABSTRACT

The pyrolysis and liquefaction yields of six coals from Alberta, Canada, have been found to be sensitive to variations in their corrected H/C ratio. The carbon and hydrogen content of the coal is corrected for carbon that evolves as carbon dioxide and hydrogen that evolves as excess water, as observed from Fischer-Shrader assay. The corrected H/C ratio is assumed proportional to the amount of hydrogen available from the coal to produce stable products. This ratio correlates with the yield of tars plus light oils observed during pyrolysis when no excess hydrogen is available. During coal liquefaction, atomic hydrogen can also be provided by hydrogen gas, the carbon monoxide shift reaction, and/or solvent. An evaluation relating this available hydrogen (Ha) to coal products is presented and demonstrated to correlate with observed pyrolysis and batch autoclave conversions. Conditions include pyrolysis (Ha = 0) and reactions with solvent and carbon monoxide at 400°C (Ha = 0.45); solvent, hydrogen gas, and iron oxide catalyst at 430°C (Ha = 0.45); solvent, carbon monoxide, and potassium carbonate catalyst at 400°C (Ha = 0.80); and solvent, hydrogen, and potassium molybdate catalyst at 400°C (Ha = 1.10).

The reaction model is based on the disproportionation of hydrogen in particulate coal into products and residue. Hydrogen available from sources other than coal (Ha) results in less hydrogen being required from residue and, therefore, higher Ha values result in higher conversions.

The correlation enables the determination of potential conversion and liquid plus gases yield from coal elemental and assay data. Since varying the hydrogen availability (Ha) affects conversion, the required operating conditions to give a desired conversion level can also be determined. Coals with low corrected H/C ratios responded dramatically to increases in Ha. However, they reached lower conversions than coals with a high corrected H/C ratio.

PRÉSENTATION 9

LES EFFETS DE L'HYDROGENE DU CHARBON SUR LA CONVERSION PAR PYROLYSE ET PAR LIQUEFACTION

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RÉSUMÉ

On a constaté que les rendements de la pyrolyse et de la liquéfaction de six charbons albertains (Canada) sont sensibles à l'évolution du rapport H/C redressé. La teneur en carbone et en hydrogène du charbon est redressée dans le cas du carbone qui devient de l'anhydride carbonique, et de l'hydrogène qui devient de l'eau excédentaire, comme on l'a constaté lors de l'essai Fischer-Shrader. On suppose que le rapport H/C redressé correspond à la quantité d'hydrogène disponible dans le charbon pour produire des produits stables. Ce rapport corresponde au rendement des goudrons complété par les pétroles légers, observé lors de la pyrolyse, en l'absence d'hydrogène excédentaire. Lors de la liquéfaction du charbon, de l'hydrogène atomique peut également être fourni par le gaz d'hydrogène, par la réaction au déplacement de l'oxyde de carbone et/ou par le solvant. Une évaluation établissant un rapport entre cet hydrogène disponible (Ha) et les produits du charbon est présentée et on démontre que celle-ci correspond à l'observation de la pyrolyse et de la conversion en autoclave. Les conditions comprennent la pyrolyse (Ha = 0) ainsi que les réactions avec solvant et l'oxyde de carbonne à 400°C (Ha = 0,45); avec solvant, gaz d'hydrogène et catalyseur d'oxyde de fer à 430°C (Ha = 0,45); solvant, oxyde de carbone, et catalyseur de carbonate de potassium à 400°C (Ha = 0,80); et solvant, hydrogène, et catalyseur de molybdate de potassium à 400°C (Ha = 1,10).

Le modèle de reaction est basé sur une modification de la proportion entre l'hydrogène du charbon particulaire et les produits et résidus. L'hydrogène ajouté réduit la quantité d'hydrogène requise à partir des résidus et les valeurs Ha supérieures donnent donc des niveaux de conversion plus élevés.

La corrélation permet de déterminer le potentiel de conversion et le rendement liquides et gaz, à partir des données concernant le charbon, les éléments du charbon et les essais. Comme la variation de la disponibilité d'hydrogène (Ha) affecte la conversion, les conditions d'exploitation permettant de réaliser un niveau de conversion souhaité peuvent également être déterminées. Les charbons ayant de faibles rapports H/C redressés ont réagi de façon draconienne aux relèvements de Ha. Toutefois, dans les conditions produisant une valeur Ha élevée, ils ont donné des conversions inférieures à celles des charbons ayant un rapport O/C redressé élevé.

COAL HYDROGEN EFFECTS ON PYROLYSIS AND LIQUEFACTION CONVERSION

INTRODUCTION

The ultimate aim of coal liquefaction is to produce environmentally clean liquids, preferably distillate, from coal while consuming the least amount of expensive hydrogen. However, there are no simple means of predicting conversion and yields from analysis data. Also, the mechanism and models that have been proposed by which coal goes to asphaltenes, to oils, etc. are complex and treat the coal liquefaction reaction as if no solvent or reducing gases were present. In the following sections, a coal disproportionation reaction model, which includes a parameter for hydrogen added due to processing conditions, is presented and compared to conversion data of six Alberta coals reacted at five different liquefaction conditions.

Conversion of subbituminous and bituminous coals to tar and light oils during low-temperature distillation at 500°C has been found to be related to the hydrogen-to-carbon ratio (1) and the hydrogen content (2) of the original coals. In both studies, coal rank influenced the correlations. The Alberta coals in this paper are uniquely different from the U.S. and Canadian coals (mostly from eastern Canada) of these previous studies.

EXPERIMENTAL

Extensive tests have been performed on six Alberta, Canada, coals in one-litre batch autoclaves by the Coal Research Department of the Alberta Research Council (3). The batch autoclaves were charged cold, heated to temperature, held at temperature for the desired time, cooled, and discharged. Conversion was determined by Soxhlet extraction. Five series of conditions, where coal was the only variable for each series, were selected for evaluation (Table 1).

Elemental and Fischer-Shrader Assay analysis data (4) were also provided by the Coal Research Department analysis group (Table 2). All data on these tables are on a wt % maf coal basis. The corrected or effective carbon (c-C) and hydrogen (c-H), and molar H/C ratio (Hc) for each coal were calculated by subtracting the hydrogen and carbon lost as water and carbon dioxide during low-temperature pyrolysis. The amount of chemically bound water and carbon dioxide was determined by the assay analysis. The loss of carbon dioxide reduces the amount of original coal carbon that could be found in organic products, while the water reduces the amount of coal hydrogen that is available to reduce coking. The oxygen lost by pyrolysis accounts for 68% to 81% of the original maf coal oxygen. The molar H/C ratio (Hr) of the char was calculated from the char elemental analysis. The empirical formula which relates the H/C ratio to heteroatom content was determined for the char. The oxygen content of the char was reduced to a level no greater than the original coal oxygen minus the oxygen in the carbon dioxide and water lost during coal pyrolysis. The resulting char elemental data were then normalized. This introduces a small error, since the assay products other than char, water, and carbon dioxide, contain oxygen. As will be observed later, the important values are H/C ratios and the coal carbon content. However, formula weights are required to adjust yields for heteroatom content. For these coals the averages were 13.5 gm/formula and 0.41 for residue FWr and H/C, respectively. The H/C ratio of the assay organic products (o-H/C) was estimated by difference using the corrected coal and char data, that is, corrected coal carbon or hydrogen values minus the char carbon or hydrogen values.

RESULTS AND DISCUSSION

Coal conversion

Conversion has been found to be dependent on processing conditions, reaction temperatures, and residence times. In rapid heat-up experiments (5), conversion has been observed to be very rapid, resulting in the initial depletion of solubilized reactant gases (CO relative to H_2) and hydrogen donor solvent components in the initial 10 minutes. This is followed by the stabilizing of the solubilized gas composition and rehydrogenation of solvent hydrogen donors (6). Therefore, liquefaction will be considered to be a two-step reaction: 1) decomposition of particulate coal in the presence of hydrogen donors at specific conditions to yield solubles and gases; and 2) the reaction of primarily solvent but also coal products. This makes only the initial reactants important for the first step. This is similar to a previous study which correlated coal conversion at constant conditions with the initial coal parameters (7) and mechanism studies (8, 9). However, in this paper, coal elemental and pyrolysis data will be used and a parameter will be included that is dependent on processing conditions.

The pyrolysis or liquefaction of coal is assumed to consist of three primary reactions:

1. Decomposition: $\text{Coal} \rightarrow 2R. + H_2O + CO_2$
2. Hydrogenation to solubles: $R. + H \rightarrow RH + R.$

3. Polymerization to residues: R. + R. → R-R

Overall Coal → Residue + products + inert gases

Reaction 1 occurs at low temperatures (it is kinetically rapid at about 360°C) and results in the production of considerable amounts of water and carbon dioxide. The Alberta coals discussed in this paper lose 15 to 19 wt % of their mass as water plus carbon dioxide. Smaller amounts of CO and other gases are produced. At higher temperatures, carbon-carbon bonds can break, depending on their bond strengths (10). Reaction 1 is the driving force, causing coal to form reactive intermediates. The reactive intermediates, if not stabilized, result in char or residue formation.

The hydrogen released as highly stable water is not available to stabilize radicals and therefore reduces the effective hydrogen content of the original coal. The carbon released as carbon dioxide reduces the amount of carbon that can be bonded to hydrogen as hydrocarbons. The net effect on pyrolysis or distillation yields is to decrease the maximum obtainable yield of hydrocarbons to 81-85 wt % (plus consumed hydrogen) for Alberta coals. However, the maximum amount of oxygen in the hydrocarbon products is reduced to 19-31% of the original coal oxygen.

The availability of hydrogen determines the extent of Reaction 2. The only source of hydrogen would be the coal itself during pyrolysis. During the initial stages of liquefaction, the unsolubilized, solid coal would also be the primary source of hydrogen (10,11). As fragmentation of the coal occurs, solvent hydrogen, hydrogen gas, and CO-water could also act as a source of hydrogen. This decreases polymerization (reaction 3) and also increases the amount of hydrogen in the remaining unconverted coal, since less is abstracted. The products (fragments stabilized by hydrogenation) during liquefaction include solubles, tars, light oils, and organic gases. Reaction 3 is the default reaction by which the reactive intermediates polymerize into large molecules (char, residue, or insoluble organic matter) if no excess hydrogen is available from coal or other sources.

Hydrogen Content of Products

The hydrogen content of coal products is related to the product fraction to which it belongs. Soluble but non-distillable preasphaltenes, asphaltenes, and oils have been defined by their hydrogen and oxygen content into solubility regions (12). Essentially all of this material has an atomic H/C ratio above 0.63, which equates to 4.5-5 wt % hydrogen at oxygen contents of 10-0 wt %, respectively. An H/C value of 0.63, therefore, represents a minimum value for a material to be soluble.

Insoluble organic matter (IOM or residue) has characteristic hydrogen contents of less than 5 wt % (9). The hydrogen content of the pyrolysis char obtained from the Alberta coals in this paper is only 3.8 wt % (the average H/C ratio is 0.41). In the correlation of tar yields with the H/C ratio of 12 Canadian coals (1), the intercept H/C value of under 0.5 at zero per cent tar yield represents a minimum char H/C ratio. In the correlation of the hydrogen content of over 70 U.S. coals with tar yields, intercept values of under 4.4 wt % hydrogen (depending on coal rank) were obtained.

The hydrogen contents of tars produced during pyrolysis are typically over 8 wt %, with an average H/C ratio of 1.3 (1) and, if molecular weight differences are considered, are unique from the hydrogen content of the non-distillable soluble fractions produced during liquefaction (12). The calculated H/C ratio for tars plus organic gases for the Alberta coals ranges from 1.2 to 2.0 (see Table 1).

In order to relate pyrolysis yields of organic products (tar, light oils, and organic C1-C6 gases) to liquefaction yields of organic products (total solubles plus organic gases), an average product H/C ratio (Hp) can be used. At low and high conversions, nearly constant values are obtained, as seen in Figure 1. The initial conversion of 19 wt % is due to the evolution of water and carbon dioxide as determined by pyrolysis. For this example, pyrolysis organic products with an average H/C ratio of 1.67 at a yield of 5 wt % of maf coal are assumed to be produced during liquefaction. The subsequent production of solubles during liquefaction with an H/C ratio of 0.63 (minimum hydrogen consumption) greatly decreases the Hp value from 1.67 to 0.77 as conversion increases to 50%. However, at typical liquefaction conditions, conversions of 50 to 95 wt % are observed, and the value of Hp remains relatively constant (decreasing from 0.77 to 0.70). This example of the relationship of the average product H/C ratio to conversion illustrates that, to cover the entire range of conversions, a changing value for Hp must be used. However, at low or high conversion, an average value may be assumed.

Reaction Model

When coal is reacted to form products, the carbon and hydrogen contents of the coal must be equal to that of the coal products minus the hydrogen added by donors other than coal. The following equation, balancing hydrogen and carbon in the overall reaction, becomes valid:

$$Tc{*}Hc = Pc{*}Hp + (Tc\text{-}Pc){*}(Hr\text{-}Ha) \qquad \text{Eq 1}$$

where for carbon:

Tc = moles of coal carbon per 100 gms of maf coal corrected for carbon lost as CO_2
Pc = the total moles of carbon in the other products
Tc-Pc = the moles of carbon in the residue;

and for hydrogen:

Hc = the effective molar H/C ratio of the coal (corrected for water hydrogen and CO_2 carbon)
Hp = the molar H/C ratio of the other products (solubles, liquids, organic gases, etc.)
Hr = the molar H/C ratio of the residue
Ha = the amount of hydrogen provided by the solvent and/or gases which reduces the need for coal hydrogen expressed as hydrogen per residue carbon atom.

The location of the Ha value in Equation 1 is significant. The Ha value expresses the amount of hydrogen available from solvent and reducing gases to stabilize radicals formed while coal solubilizes. According to Equation 2, coal radicals require hydrogen to become soluble, and solubilization must occur initially at the surface of the coal particle. Abstraction of hydrogen from other than residual coal particles decreases the abstraction of hydrogen from these particles. Therefore, the value Ha has been defined as the hydrogen content of the surroundings that is available, divided by the molar carbon content of the residue.

Conversion is equal to 100 minus residue, and the residue is related to its carbon content by its formula weight (where the moles of carbon are equal to one), as seen in Equation 2.

$$\text{Conversion} = 100 - (FWr)(Tc\text{-}Pc) \qquad \text{Eq 2}$$

FWr = the average formula weight of the residue, where the carbon is set equal to one:

$$C_1H_{.41}O_{.07}N_0S_0 = 13.5$$

Solving Equation 1 for the moles of carbon in organic products (Pc), insertion into Equation 2 and rearrangement to a Y = mX + b form results in Equation 3.

$$\begin{array}{l}\text{Conversion}\\ \text{\%maf coal}\end{array} = \overbrace{100 - (FWr)\,Tc\left[1 + \frac{Hr\text{-}Ha}{Hp\text{-}(Hr\text{-}Ha)}\right]}^{\text{Intercept}} + \overbrace{\left[\frac{(FWr)Tc}{Hp\text{-}(Hr\text{-}Ha)}\right]}^{\text{Slope}} Hc \qquad \text{Eq 3}$$

Equation 4 relates the total organic products (net liquid plus organic gases) to conversion minus pyrolysis-produced water and carbon dioxide.

$$\text{Products} = \text{Conversion} - (\text{assay wt \% } CO_2 + H_2O) \qquad \text{Eq 4}$$

Equation 3 has been restated to enable the plotting of conversion versus the effective coal H/C ratio (Hc). Both the slope and intercept are dependent on the H/C ratios of the residue and products as well as the hydrogen available from non-coal sources and the formula weight of the residue. However, at constant reaction conditions, where only the coal is varied, the slope and intercept are assumed constant.

Applying Equations 3 and 4 to assay pyrolysis yields resulted in a reasonable correlation of tar yields with the effective hydrogen-to-carbon ratio of the coal, as seen in Figure 2. The average product H/C ratio used was 1.45 (essentially the average for the Alberta coals; see Table 2). As noted in an earlier correlation for U.S. coals (2), correlations to tar yields are highly sensitive to the coal hydrogen content. In Figure 2, it can also be seen that for Vesta coal (V), the high product H/C ratio decreases the observed tar yield.

Use of the principles in the model presented, which includes factors for correcting the coal hydrogen and carbon content and a maximum yield due to loss of mass as water and carbon dioxide, improves the overall correlation previously reported (1) for Canadian coals. If the coal hydrogen content is corrected for hydrogen lost in water and divided by the fixed carbon plus 0.2 times the volatile matter (the denominator corrects for heteroatom content), the tar yields from semi-anthracite to lignites correlate. However, the Alberta coals are unique in that they produce much more tar at lower coal hydrogen values than the eastern Canadian coals. The difference may be related to the low hydrogen content of the char obtained from Alberta coals relative to other coals. However, this has not yet been tested.

The prediction of pyrolysis tar yields using data obtained by pyrolysis is not very useful. However, the main reason for discussing this correlation is to validate the reaction model and Equations 3 and 4. Also, the principles involved can be used to correlate data from coals of different rank. The ability to estimate liquefaction conversion and how conversion is related to operating conditions does represent a step forward.

Plotting liquefaction conversion versus the corrected coal H/C value at constant conditions for these coals with similar chemical, water and carbon dioxide contents, resulted in plots such as Figure 2 at the top. The various coals were reacted at 400°C with carbon monoxide, water, and 2.6 gms of potassium carbonate in anthracene oil solvent. The theoretical conversion line was calculated using Equation 3, where FWr = 13.5 and Hr = 0.41. The average product H/C ratio was set at 0.70. The available hydrogen value (Ha) was varied until a best fit was obtained. It was also verified that the sum of the observed residue, calculated product yield, carbon dioxide, and water approximated 100%. As observed in the plot, the experimentally determined conversions are within error of tests. The calculated product yield (Eq 4) can be compared to the observed yield of liquids plus gases (Fig. 2). The experimental data points are approximated by the calculated values. Reactions in anthracene oil at 400°C produce few organic gases, and therefore the product yield does not include the C_1-C_6 gases. The other data were evaluated for each condition in a similar manner and resulted in similar correlations with conversion. The Ha values determined for the other conditions are presented in Table 3.

A comprehensive diagram of the effects of the corrected coal H/C ratio on conversion and the amount of hydrogen added is depicted in Figure 3. In pyrolysis tests where the Ha = 0, the conversion and yields were very dependent on the average product H/C ratio, while in liquefaction the Ha value is more important. The model also predicts that if only a small amount of additional hydrogen is available (Ha = 0.1), conversion is greatly increased. The influence of small amounts of hydrogen on conversion has been reported for one coal (11). Coals with low H/C ratios are influenced the most.

For liquefaction, coal conversion was dependent on the ability of solvent, reducing gases, and catalysts to make hydrogen available. Different operating conditions produced the Ha lines at 0.3 to 1.1 for the six coals, resulting in the ranking shown in Table 3.

The emulsified KMo catalyst was effective in making hydrogen available to the decomposing coal, while the Fe_2O_3 catalyst at 470°C resulted in the lowest hydrogen availability. Potassium carbonate catalyst was almost twice as effective as the solvent and reducing gas alone. By using the coal reaction model (Eq 3) and using average values for the Alberta coals, the effective coal hydrogen content can be related to conversion and the amount of hydrogen available (Ha) at different operating conditions (see Fig. 3 and 4). In Figure 3, the average product H/C ratio (Hp) was set at 0.7 and 1.45 or 2.00 to depict liquefaction and pyrolysis conversion data, respectively. As discussed earlier for liquefaction, the value for Hp varies with conversion, and at conversions under 50% the error gets large. However, none of the operating conditions evaluated resulted in Ha values less than 0.35 (except pyrolysis). Figure 4 was plotted using calculated Hp values to illustrate the availability of hydrogen at different operating conditions and its effect on conversion. The model indicates that, for a low-hydrogen Alberta coal, other techniques may be required to increase conversion over 84%. However, Alberta coals with H/C values of over 0.6 result in excellent conversions and are relatively insensitive to operating conditions.

The model can also be used to better assess other types of processes presently being tested. Hydropyrolysis of coals with an Hc of 0.6 should result in relatively high conversions, as would short contact time liquefaction, with little hydrogen consumed. Coals with low H/C ratios of about 0.5 would require conditions where excessively high amounts of hydrogen were available to reach even 90% conversion levels. The Exxon Donor Solvent process is based on increasing the Ha value by using an externally hydrogenated solvent. However, compared to high-rank coals, the lower rank coals required more stringent conditions due to there being less effective hydrogen in these coals. Higher, more consistent conversions have been obtained by stirring the reactants (coal, solvent, CO, and water) overnight prior to reaction (13). The fact that small increases in Ha can have a large effect on conversion makes this observation more understandable. If only small amounts of gas and solvent penetrated the coal particles, more hydrogen would be available during the critical initial stages of coal decomposition.

The difference in reproducibility of liquefaction conversions for Alberta coals with low- and high-hydrogen contents is also more understandable. For a low-hydrogen coal, minor differences between tests (different mixing rates, solvent or gas penetration of the coal particle, and/or initial coal particle size), causing differences in the amount of hydrogen available from the solvent and reducing gases, could cause large differences in the observed conversion. As noted earlier and as predicted by the model, conversion data for low-hydrogen coal is much more difficult to reproduce than conversion data for higher hydrogen coals. This relationship also indicates that for basic studies, a low-hydrogen coal is an optimum choice, since it is much more sensitive to reaction conditions (see Fig. 3).

CONCLUSION

The results indicate that coal pyrolysis and the initial stages of coal liquefaction can be modeled by a simple decomposition reaction where the effective coal hydrogen is redistributed to produce residue, liquid, and gaseous products. The maximum organic product yield from a given coal is derated by the amount of inert material (water and carbon dioxide) that is obtained from low-temperature distillation. Increasing the availability of hydrogen from solvent and gases by changing reaction conditions decreased the demand on residue hydrogen and therefore increased the production of organic products. Hydrogenation and cracking reactions of solubilized coal products to produce a greater yield of distillable products (Step 2) would be separate from the initial coal decomposition and could be modeled separately.

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TABLES

Table 1 – Coal study operating conditions*

# of tests	Charge Pressure—gas (psi)		Reaction temp.—time (°C)	(min)	Total water (gm)	Catalyst—gm	
8	1000	CO	400	30	34	None	
15	1000	CO	400	30	34	K_2CO_3	2.5
16	1500	H_2	430	30	7-20	KMo**	2.6
15	1500	H_2	430	45	4-16	Fe_2O_3	1.5
13	1750	H_2	470	0	4-15	Fe_2O_3	1.5

* *Coal charged = 50 gm maf; anthracene oil = 126 gm*
Equipment: 1 litre, stirred autoclave

** *Potassium molybdate was dissolved in water and emulsified with the charge slurry*

Table 2 – Coal elemental and analysis data

Coal type: Coal abbreviation:	Vesta VES	Smoky Tower SMT	Fox Creek FCK	Judy Creek JCK	Highvale HVL	Ardley ARD
Elemental, wt % maf coal:						
Carbon	74.44	75.09	75.63	75.11	75.40	75.68
Hydrogen	4.95	4.50	4.25	4.09	4.10	4.15
Nitrogen	1.50	1.72	1.90	.79	1.00	1.17
Oxygen	18.48	18.16	17.64	19.72	19.30	18.55
Sulphur	.63	.53	.58	.29	.20	.45
Molar H/C	.798	.719	.674	.653	.653	.658
Corrected for pyrolysis water and carbon dioxide:						
Carbon	72.10	73.44	73.93	72.96	72.85	73.88
Hydrogen	3.35	3.49	3.17	3.12	3.01	3.00
H/C	.641	.570	.515	.514	.496	.488
Fischer Assay analysis, wt % maf coal:						
Char	69.6	71.6	74.7	74.6	74.5	75.1
Char elemental, wt % maf coal:						
Carbon	62.00	61.70	66.36	64.75	67.37	66.62
Hydrogen	2.13	2.16	2.22	2.20	2.26	2.30
Nitrogen	1.48	1.54	1.03	.82	.93	1.07
Oxygen	3.44	5.68	4.49	6.27	3.81	4.60
Sulphur	.37	.34	.33	.30	.12	.27
H/C	.413	.420	.402	.401	.403	.414
Formula weight	13.44	13.92	13.50	13.82	13.26	13.52
Total gas	14.2	12.6	12.2	13.6	14.4	12.2
Tar + Lt oils	5.2	7.1	5.3	5.1	3.0	3.2
Water	9.9	9.1	9.7	8.7	9.8	10.3
Carbon dioxide	8.58	6.03	6.22	7.86	9.32	6.59
% coal oxygen lost*	81.38	68.69	74.52	68.20	80.25	75.19
Non-residue H/C**	2.04	1.36	1.51	1.34	1.64	1.17

* *Oxygen lost in carbon dioxide and water*

** *Represents the H/C ratio of the organic products; tar plus organic gases*

Table 3 – Changes in hydrogen available for coal liquefaction at various conditions

Condition	Temp. (°C)	Ha
KMo + H_2	400	1.10
K_2CO_3 + CO-H_2O	400	0.80
Solvent + CO-H_2O	400	0.45
Fe_2O_3 + H_2	430	0.45
Fe_2O_3 + H_2	470	0.30
Coal only	500	0.00

FIGURES

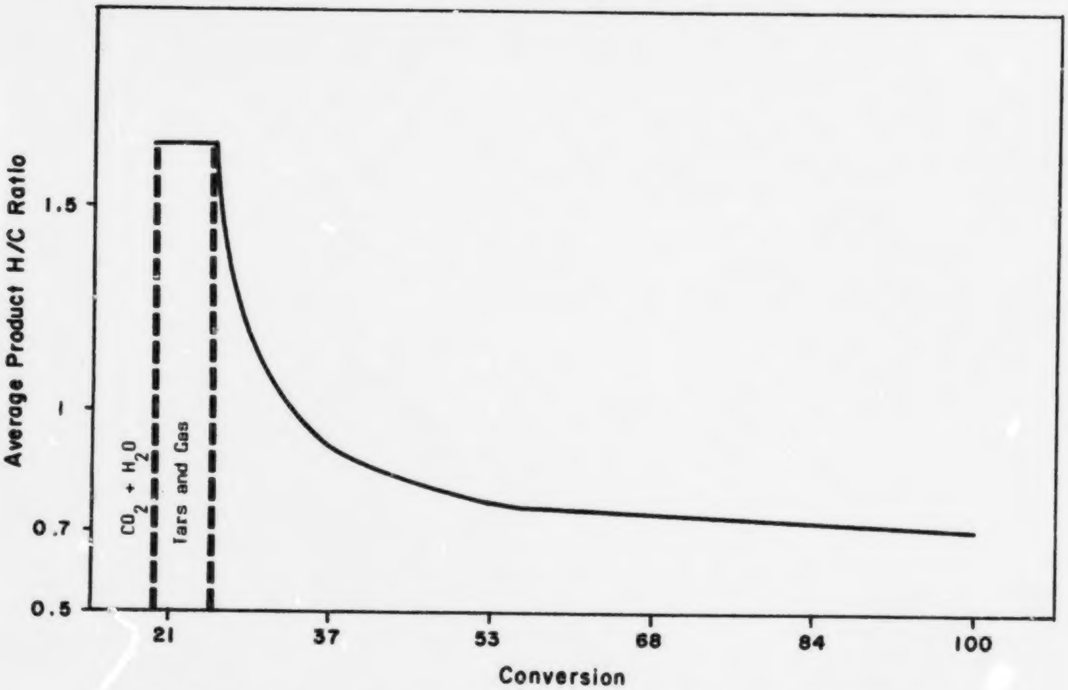

Fig. 1 – Example of the change in the average product H/C ratio with conversion

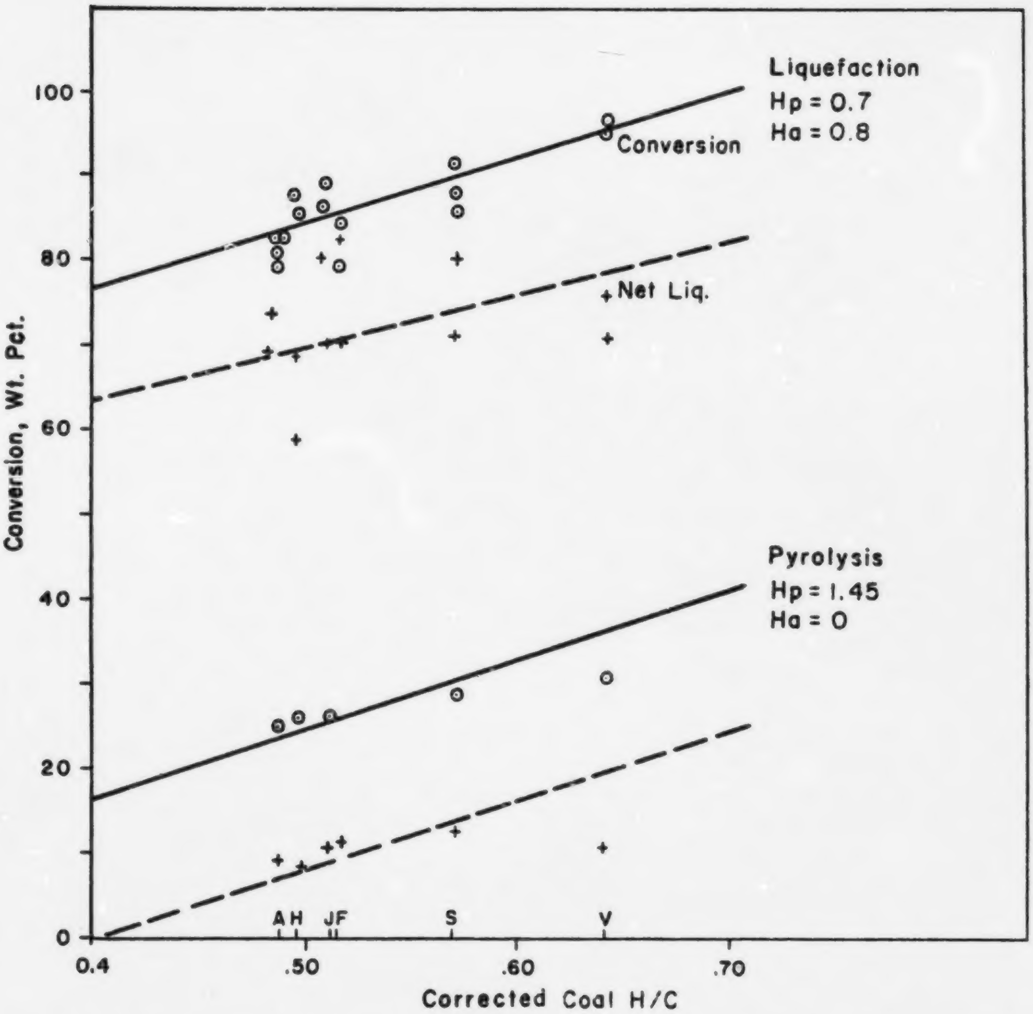

Fig. 2 – Typical fit of the observed and calculated conversion (—) and product yields (—). The coals were liquefied in anthracene oil with potassium carbonate and CO-water. The pyrolysis data were obtained from Fischer Assay analysis. Hp equals the average product H/C ratio, while Ha represents the amount of hydrogen available to the coal products from solvent or reducing gases.

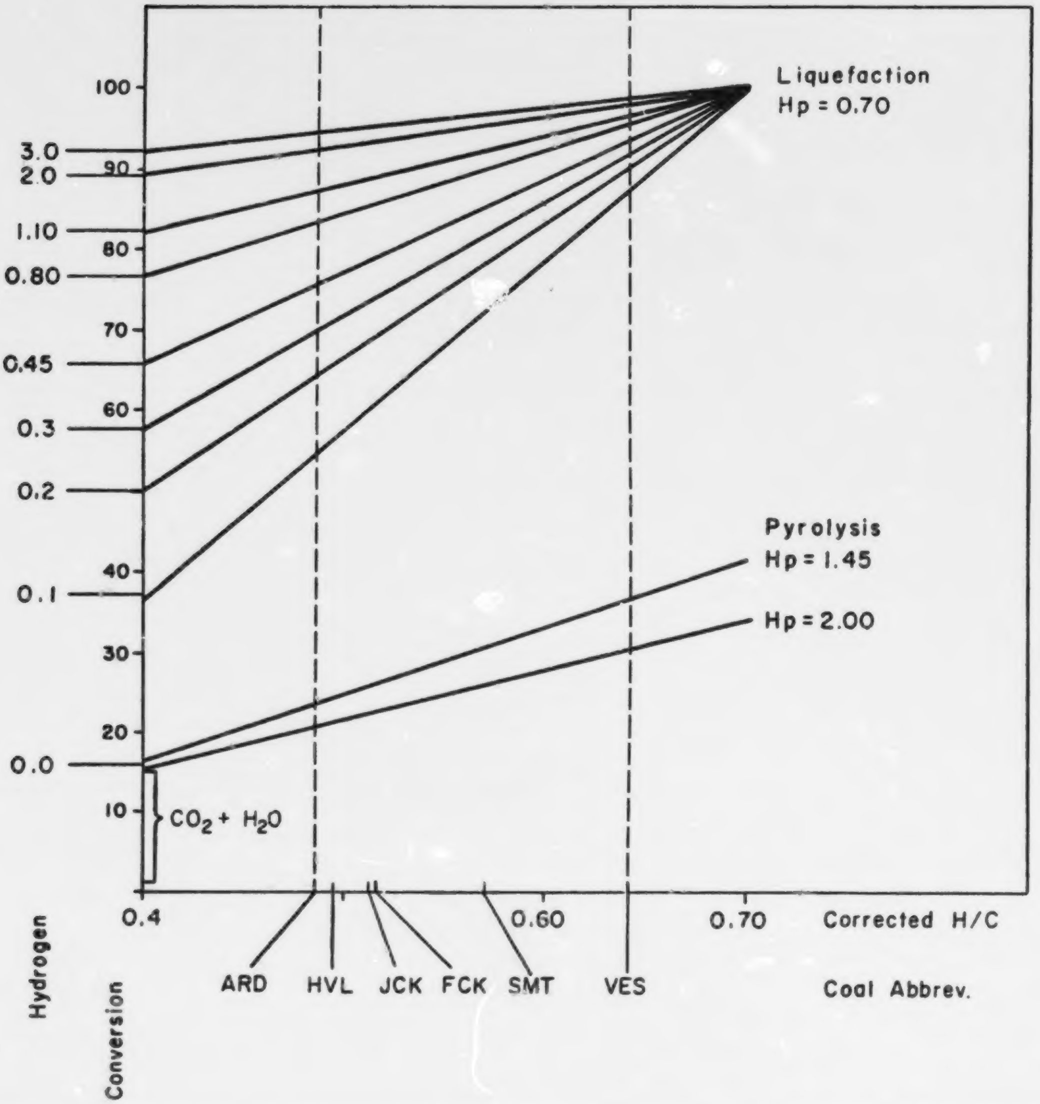

Fig. 3 – The relationship of available hydrogen (Ha) and conversion values to the effective coal H/C ratios. The ratios of the coals studied are indicated. Hp equals the average product (liquids and C1-C6 gases) H/C ratio.

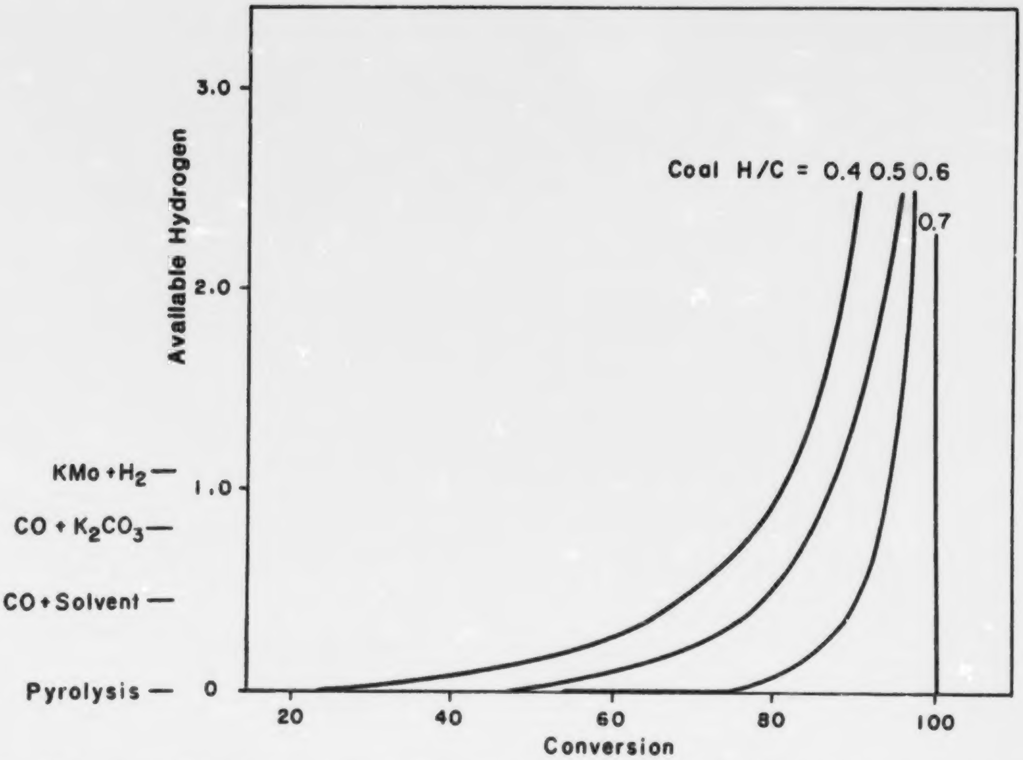

Fig. 4 – The effect of available hydrogen on the conversion of Alberta coals with different effective molar H/C ratios. Included are processing conditions which have provided various levels of available hydrogen.

SESSION II

DISCUSSION

MODERATOR: M.P. duPLESSIS, ALBERTA RESEARCH COUNCIL

REEVE (CANMET): I have a couple of questions for Mr. Satake based on his very interesting paper. The first one, a very quick question perhaps, but you mentioned the Nippon Brown Coal Company running the plant in Australia and then the Nippon Coal Oil Company running the NEDOL plant. Is there any relation at all between these companies or are they completely separate?

SATAKE (NEDO): Officially there is no relation, but some industrial companies have joined both groups.

REEVE (CANMET): Secondly, a question with respect to the Victoria plant. Brown coal in Australia, as far as I can recall, is very high in moisture and low in ash. I believe less than 1%. Would it be possible not to include the de-ashing unit in the circuit? In the diagram of the 50 tons per day unit, you showed in the second part of the diagram a de-ashing unit. Because of the low ash content of the Victoria brown coal would it be possible to eliminate that, or minimize it?

SATAKE (NEDO): Minimize, the ash content is from 1-3%, it is very low.

REEVE (CANMET): I thought it was even lower than that. And perhaps I could ask you a third question also. When you were describing the NEDOL plant you talked about the continuous pilot plants leading up to the design of that plant and you gave a wide range of pressures, from I think 9 up to about 20 MPa. Can you give us any closer feeling at what pressure the NEDOL plant will operate?

SATAKE (NEDO): We plan to operate at about 150 atmospheres.

YAN (MOBIL): I have several very short questions. First of all, for Dr. Ogle. I was very interested in seeing that the first objective of IEA was to do an evaluation of evolutionary improvements or something to that effect. I just wonder, why not try to put some more emphasis on development of revolutionary process concepts, rather than re-evaluation of evolutionary processes. I cannot help but be impressed that we have developed about the same process everywhere, that is, they are all about the same. What we really need is new revolutionary concepts for liquefaction rather than everybody doing pretty much the same thing. What's your comment? Maybe the IEA is a good place to start.

OGLE (OERD/EMR): Not having been involved in that particular exercise with the IEA I can only speculate. But let me say this. I think that there are probably better opportunities for cooperation in the nearer term type processes with regard to evolution as opposed to revolution. I hope we will hear more today or rather tomorrow about the more revolutionary work that is going on. But I would suspect that because it is more revolutionary it is probably more difficult to maintain a cooperative international effort. The time will perhaps come when that will be more possible.

YAN (MOBIL): Yes, I am not really actively participating in these kinds of things, but I do feel what we really need is a new concept, new ideas. Everybody is working on something on the shelf, which is really not very fruitful in my opinion. I have a second question for Dr. Neef about the new reactor design. I thought that was very interesting. I think this is a little more than evolutionary, with a L-to-D ratio of 10,000. May I ask what size of diameter that really turns out to be?

NEEF (KFA): The actual length of the tube is 250 metres.

YAN (MOBIL): Thank you, I can calculate the diameter. Is it a multiple pass tube?

NEEF (KFA): Yes, it's multiple pass, it is just going around. But you see I'm not able to reveal the design details here. The only thing I can tell you is that you can have it in five parts. I hope they (Saltzgetter and Imhausen) will produce good results over the next year. I would certainly not be the first to publish them because they should publish them first.

YAN (MOBIL): In that process, do you still use catalysts?

NEEF (KFA): Yes.

YAN (MOBIL): In a slurry form still?

NEEF (KFA): I think so, but I'm not quite sure. We use catalysts there, but since the test program has not been evolved, it's very difficult to say.

YAN (MOBIL): I know you don't have the data yet, but have you heard any rumour about operability?

NEEF (KFA): Well, I think the industrial companies who invented the process claim a high operability based on their experience with high pressure polyethylene manufacturing. As I told you, we had better wait for another year.

YAN (MOBIL): That's all right. I want one last question to Dr. Knudson. I am impressed with your very nice curve of hydrogen versus oxygen coordination. It is very much like a phase diagram. Could you tell me how this was developed? I am always fascinated by phase diagrams like this.

KNUDSON (UNIV. OF NORTH DAKOTA): You get a lot of data, and you put it into a computer, and the computer starts working on it and you look at some of the garbage a computer can put out, and you get maybe 50-60 graphs. All of a sudden you look at it and some of it starts making sense. We actually started out in a very difficult manner. It's work between Dr. Boltisburger, University of North Dakota and Dr. Wholsy and myself. They did a lot of analysis and gave us back a lot of data, and I started putting process conditions on it. But as I was doing that, all of a sudden, things started falling together. We did hydrogen to carbon and OH phenolic content first. Well, you can't find as much data in the literature. Actually, the correlation gets better as you go from the fancy NMR data (and I hope there are not too many NMR people here) back to simple hydrogen content. It does not get any worse if you use OH or oxygen content on the bottom scale. That line is a very definite line. On each side of that line you will have asphaltenes and pre-asphaltenes. I think we have about 250 points that consist of 77 on one side of the line and 77 on the other, as well as half a dozen up there from Boltisberger's work and from literature data. We have added a couple of more sets of data too. Furimsky's work does plot. There is a high molecular weight asphaltene region above the oil region, so there is a molecular weight factor in there. But if you're only looking at coal liquefaction and not at petroleum products, you're safe.

MIKHLIN (SNC): I would like to question, if I may, Dr. Ogle. You mentioned that there was a kind of consortium which was approved by the provincial government in connection with coal liquefaction. Could it be made a little more clear, if possible? Or, perhaps it is too early to say.

MODERATOR (ALBERTA RESEARCH COUNCIL): Can you repeat the question, I didn't quite get that? Maybe you heard it Ian and can repeat the question?

OGLE (OERD/EMR): I think what Dr. Mikhlin is asking about is a reference I made to continuation of discussions between certain Canadian parties and certain West German parties outside of the S&T umbrella which have resulted in a specific proposal that has now received approval. I can answer one part of that quite comfortably. I believe that Dr. Fritz Boehm is in the room. Perhaps he would also like to make some comments. The proposal that I was referring to related to the Alberta/Canada Energy Resources Research Fund, which is a combined Canada/EMR/Alberta Energy Natural Resources Fund. I do not have the details of the proposal with me and perhaps if Dr. Boehm is in the room, he would like to comment.

MODERATOR (ALBERTA RESEARCH COUNCIL): Yes, could we ask Dr. Boehm to say a few words about this project?

BOEHM (CANADIAN COAL LIQUEFACTION CORPORATION): The project you are referring to consists of two parts. Part one is a feasibility study which we sublet to Kilborn Kellogg Rust roughly six weeks ago. The objective is twofold. First of all, we want to know where we stand in dollars per barrel for a specific concept for coal liquefaction of Alberta subbituminous coal. The second objective of the feasibility study is to determine where we really would aim this coal-oil in the spectrum of conventional oil, syncrude from tar sands, and syncrude from heavy oils. So we want to know where the optimum place is for coal-oil in Alberta and Canada. The second part of the project, which may be at least for us, the more important part, is building a six ton per day pilot plant based on the experiences gained with the Saarberg pilot plant and research work by the Alberta Research Council. So the concept basically, and I don't want to go into too much detail here, consists of coprocessing using a two-stage direct liquefaction process with CO steam in the first stage and hydrogen in the second stage. The front end, i.e., de-ashing will be done hopefully with the help of coal agglomeration and at the other end will be a fluidized-bed combustion unit to take up the residue. I would like to stress that the process was developed in many discussions with all parties concerned. We feel that we have a very optimum process. It's an evolutionary process, not a revolutionary process, but I think we have a very good one here. We are convinced that our feasibility study will bring us into the range of competitiveness in the oil market. If I say that, I refer certainly not to imported oil but to oil from the tar sands and from the frontiers Mr. Ogle showed us in his slide. Maybe I should mention that the Canadian Coal Liquefaction Corporation is really working very closely with the Alberta Research Council and the Alberta government. We will work very closely with the federal government and industry. There are participants from industry involved, and several others have approached us and want to participate. I would say the financing of both parts of the project is basically in my opinion secured. So we hope that in two years we will have a pilot plant operating in Alberta. Thank you.

KELLY (CANMET): Dr. Neef, you mentioned earlier, if I understood correctly, that Rheinbraun would be starting an R&D program on coprocessing, specifically with lignite. In view of Dr. Boehm's statement, how does that fit in with, for example, Saarberg's potential involvement with the Canadian Coal Liquefaction Corporation?

NEEF (KFA): I think they are two sides of a coin. These companies operate independently and what we try as coordinators of research is to avoid them doing the same thing in two places.

KELLY (CANMET): Could you tell us a little about the Rheinbraun project?

NEEF (KFA): I'm terribly sorry, but that has not been approved as a project, it's a project proposal and it is too early to reveal details. But, as I have learned from discussions with Rheinbraun, they did some work on heavy residual upgrading without governmental money. As you perhaps know, they have more or less stopped their work on coal liquefaction, at least that supported with governmental money. But inside the company obviously some of the research work did go on. The test plants were still in a condition that they could be operated. So hopefully they will start by next year again with some activities which would go directly into the area of coprocessing of lignite and mineral oil-based residuals.

BOEHM (CANADIAN COAL LIQUEFACTION CORPORATION): A very short comment as to why we ended up with Saarbergwerke as our partner. By the way, Saarberg will be up to a 25% partner in the Canadian Coal Liquefaction Corporation. The reason is that we feel there is enough coprocessing experience here in Canada so that part of the exercise we can very well supply ourselves. The reason we went to Saarberg boils down to that we wanted to have an experienced operator of a pilot plant of a similar size as we envisage building here. The pilot plant itself certainly again is a compromise. We feel that 6 tons per day is a good size for scale up and gives us enough flexibility to really test the number of modifications we have in mind.

SCOTT (UNIV. OF WATERLOO): Dr. Knudson, your correlations that you're developing relating the available hydrogen to liquid yields and so on are very interesting. I think they hold promise of being very useful. I wanted to ask you, you have used Furimsky's work in developing your phase diagrams or whatever you want to call them. Some of your own work, I know, appears to be based on relatively slow pyrolysis. This is with respect to the pyrolysis results. The Alberta Research Council has, I think, done some fast pyrolysis but there are also a lot of results available from the Australian work, German Rhurgas work, and so on, on quite fast pyrolysis processes. Have you used this work in developing these correlations as well?

KNUDSON (UNIV. OF NORTH DAKOTA): As of now, I have not. I have recognized the existence of it, but as of now the one Bureau of Mines paper which is a very old one, and actually was published way back in 1944, had approximately 77 analyses in it. That was all Fischer Assay type slow pyrolysis. I have been interested in trying to look at hydropyrolysis and see how it relates to that. If it does show up in that very low hydrogen consumption region, we have a low hydrogen availability, but get a very dramatic increase in yields. There is a paper by Curran on liquefaction which tends to indicate that when you have an aromatic solvent you put in just a small amount of tetralin and you get a dramatic increase in liquefaction yields. So that is present in liquefaction. But it actually says for some of these coals, for instance the Vesta and Smoky Tower, that they should act very good in flash pyrolysis too. They need very little available hydrogen to produce much larger yields of products.

I have not done that yet but I'm going to try it. I am in liquefaction and I get in trouble sometimes because some people say it's coal science.

SCOTT (UNIV. OF WATERLOO): Well, it may be that this kind of approach will explain why some of the lower rank coals give so much higher tar yields than we see from Fischer Assay.

duPLESSIS (ALBERTA RESEARCH COUNCIL): I have a short question for Mr. Satake. I was very interested to hear about his process simulator or the attempt to develop a process simulator. I wonder if he could comment on the nature of the simulator. Is it an empirical process type modelling simulator or is it based on some sort of concept of the liquefaction chemistry?

SATAKE (NEDO): This simulator was developed for the evaluation of process flowsheets. So, it is somewhat a conceptual one. We can calculate the flow rates or yields to some extent, but not completely.

duPLESSIS (ALBERTA RESEARCH COUNCIL): Is it based then on material balance data or performance data that you have developed from experimental results?

SATAKE (NEDO): Yes, material balance data are contained in this process simulator.

OGLE (OERD/EMR): I have a question for Mr. Satake. You mentioned in your presentation that you have been doing some alloy development work in relation to the new 250 tons per day plant based on development of 3 chromium-molybdenum steels as opposed to 2½ chromium-molybdenum steels. I wonder, given the fact that most of the problems with the 2½ chromium-molybdenum steels in hydrocrackers have been based on disbonding problems plus stress intensity problems where there is disbonding, if you could explain why you feel you have to go to a 3 chromium-molybdenum?

SATAKE (NEDO): I explained our supporting research programs, but the objective of this supporting research is all for commercial-scale operation. In order for the process to be economical new alloys have to be developed according to our ideas. In other words, of course we can apply 2/4 chromium alloy steel to this pilot plant but it is a little thicker than the new alloy. At the commercial stage the total reactor weight is too heavy to be transported and equipped. So, as a trial, we developed our new alloy.

SESSION III

PYROLYSIS / FUNDAMENTALS

Chairman: D. Abbott

SESSION III: PAPER 10

THE PYROLYSIS OF SOME CANADIAN COALS

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ABSTRACT

The yields of organic liquids obtained from short residence time pyrolysis in a bench-scale fluidized-bed reactor are presented. The variations of the liquid yields with temperature, residence time, particle size and reaction atmosphere were investigated. Maximum yields of liquids (16-20%) were obtained from high-volatile bituminous eastern Canadian coals. Western Canadian low-volatile bituminous coal, subbituminous coal and lignite gave liquid yields of about 8-14%. An increased liquid yield resulted when lignite was first acid washed. Some conclusions can be reached from this work concerning the use of fluid-bed technology for coal pyrolysis reactions.

**denotes speaker*

PRÉSENTATION 10

LA PYROLYSE DE CERTAINS CHARBONS CANADIENS

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RÉSUMÉ

Cette communication décrit les rendements de liquides organiques obtenus grâce à une brève pyrolyse dans un réacteur à lit fluide, à l'échelle du banc d'essai. La variation des rendements de liquides selon la température, la durée du traitement, la grosseur des particules et l'atmosphère de réaction a été étudiée. Les rendements maximals de liquides (16 à 20 %) ont été obtenus à partir de charbons bitumineux très volatils de l'Est du Canada. Le lignite, le charbon sub-bitumineux et le charbon bitumineux peu volatil de l'Ouest du Canada ont donné des rendements de liquides d'environ 8 à 14 %. On a enregistré un rendement de liquides supérieur, lorsque le lignite était d'abord lavé à l'acide et un rendement inférieur lorsqu'on a procédé à la préoxydation des charbons agglutinés. On peut tirer de ce travail certaines conclusions concernant l'utilisation de la technologie du lit fluide et les réactions de la pyrolyse du charbon.

**indique le conférencier*

THE PYROLYSIS OF SOME CANADIAN COALS

INTRODUCTION

Work on coal pyrolysis was initiated at the University of Waterloo in 1979 using a small bench-scale fluidized-bed apparatus patterned after that developed by CSIRO (Tyler, 1979). During the initial work carried out (Scott, 1980), a somewhat larger scale reactor was developed than that used by Tyler – 15 gms/hr throughput rather than 1-3 gms/hr. This larger scale was made possible by the development of a new entrained flow feeder that allowed feed rates of 5-100 gms/hr with a reproducibility of ±5% (Scott and Piskorz, 1982). In this preliminary work, the methodology and procedures were developed for the bench-scale, mini-fluidized-bed apparatus, and a series of pyrolysis tests were done on Alberta Forestburg subbituminous coal which indicated that yields of liquids comparable to those obtained by others could be realized.

In June 1981, a new program was initiated to evaluate the short residence time pyrolysis of coal at atmospheric pressure with the primary objective of determining conditions for optimum yields of liquids from a subbituminous coal (Scott, 1982). During this work, the bench-scale fluidized-bed method was improved so that better material balances were obtained, and a small stainless steel reactor was developed in place of the earlier quartz version. In fact, three coals were tested for pyrolysis behaviour, two Alberta subbituminous coals and a Nova Scotia bituminous coal, and some preliminary results were reported previously (Scott et al., 1982). The previous study reported that yields of 10%-12% (max) of hydrocarbon liquids could be obtained from Alberta Forestburg or Highvale (Wabamun) coal at optimum conditions of 650°C, one atmosphere absolute pressure in a nitrogen atmosphere and about 0.44 secs. apparent gas residence time. Additional pyrolysis tests done on Devco coal (high-volatile bituminous caking coal) indicated that oil yields of 17%-21% max could be obtained at temperatures from 650°-750°C and 0.5 sec. apparent residence time. However, operating problems with the fluidized bed were also encountered due to the caking behaviour of the coal.

Additional tests using the subbituminous coals showed that CO_2 atmosphere seemed to have little effect in increasing liquid yields, contrary to literature reports. A hydrogen atmosphere reduced liquid yields and increased gas yields.

The major analytical problems were found to be in the accurate determination of water, and in obtaining good results for the amounts of highly volatile hydrocarbon liquids produced. However, tar yields, when normalized, appeared to agree well with those of other workers reported in the literature for coals having similar H/C ratios.

The primary objective of the work undertaken during this research program is to determine the pyrolysis conditions for an atmospheric pressure fluidized-bed process which result in a maximum yield of liquid products. Initial studies suggest that these optimum conditions will be different for different coals. Further, some coals are readily processed in a fluidized-bed reactor, while others appear likely to cause operating problems if not handled correctly. In addition, reports in the literature have suggested various pre-treatments for coal which may have the effect of increasing liquid yields or minimizing operating problems. The objectives of the present work, therefore, were to screen a number of Canadian coals of widely varying character in order to determine the optimum conditions for pyrolysis, and the effects of some pre-treatments or alternative processing methods on liquid yields.

APPARATUS AND PROCEDURES

The pyrolysis tests were carried out in two sizes of reactor. The smaller of these was mentioned in the Introduction and described in a previous report (Scott et al., 1982). A second similar but larger reactor was designed to have a cyclone separator for char contained in the furnace enclosure also.

This larger fluid-bed reactor with a net volume 154.6 ml was used primarily for caking coals or to give longer residence times. Because some agglomeration always occurred in the bed, and there was some caking on the walls with these coals, the larger reactor dimensions usually allowed a run to be completed before these phenomena prevented operation. The details of this larger reactor are shown in Figure 1. The injection tube in this reactor could be air- or water-cooled if necessary to prevent plugging when caking coals were fed. Interchanging the large and small reactors allowed a wider range of residence times to be used also. Within the experimental accuracy, the yields obtained in the two reactors were the same as the same reaction conditions.

The analysis of volatile organic products continued to present a problem. If these compounds are condensed, then they will be lost in the subsequent solvent washing and evaporation steps. An attempt was made in most of the runs to measure BTX (benzene, toluene, xylene) fraction and C_6-C_8 hydrocarbons directly in a hot gas sample. However, by the conclusion of this work, it was assumed on the basis of vapour pressure calculations that most of these volatiles would not reach saturation pressure and therefore were contained entirely in the cool gas collected, so that hot gas sampling was unnecessary. Where BTX or C_6-C_8 are not reported separately in later runs, they are included in the yield of the C_4 fraction, which was calculated from the areas of the chromatographic peaks of higher molecular weight compounds than C_3 obtained in the GC analysis of the product gas employing an FID detector for high sensitivity. However, minor yields of compounds of intermediate volatility may still be unaccounted for.

In general, product analysis was carried out as described previously (Scott et al., 1982) with some improvements. A Karl Fischer titration was used to determine the water yield by analyzing the liquid condensate and all solvent washings for H_2O *before* evaporation, and correcting for a blank solvent determination. To this was added the water content of the product gases to arrive at the final total water yield. This method yielded more consistent, and higher, values for water in the products than other approaches.

In most of the results given here, tar was removed from the apparatus by washing with methylene chloride and then with acetone. In later runs, a single mixed solvent of acetone/methylene chloride was used and, subsequently, a mixed solvent of methanol/methylene chloride, inasmuch as the latter gives less interference in the Karl Fischer titration.

RESULTS AND DISCUSSION

Materials Used

In the results reported in this work, a total of eight coals were used as listed below. All samples were obtained from the Energy Research Laboratories of CANMET, Bells Corners, Ontario. One lignite, three subbituminous, and four bituminous caking coals were used. All but one of these coals were from western Canada.

Proximate analyses of the coals are given in Table 1. Ultimate analysis values are given in Table 2. The elemental and proximate analyses were done by various sources, as noted. It was observed that both proximate and ultimate analyses for the same coal from different sources often varied widely, but many of the discrepancies disappeared if the analyses were compared on a moisture- and ash-free basis.

The coals used showed a wide variation in volatile matter. As pointed out by Furimsky (1981), however, a high volatile matter value does not correlate with high liquid hydrocarbon yield for lignites or high-volatile subbituminous coals from western Canada, at least, not on the basis of the Fischer or Gray-King assay. All the coals used were relatively low in sulfur. A very large difference in oxygen content is apparent between the lower rank lignite and subbituminous coals and the higher rank bituminous coals. All the coals used except for the Devco eastern Canadian coal had a substantial ash content. Since ash content is thought to have some effect on promoting gasification reactions, this factor may be classed as a less desirable feature if maximum production of liquids is a goal.

All coals were ground and screened to $-149 + 74$ µm ($-100 + 200$ mesh) and this was used as the standard feed size unless otherwise noted, e.g., in tests to determine the effect of particle size. Most of the coals were used as received except for the lignite which had to be air-dried to about 7.0% moisture before it could be fed at a constant rate from the low-rate feeder.

Effect of Temperature

In the results given in the following sections, the definitions of *tar* and *gas* are usually consistent. In most cases, the gas yield quoted includes hydrocarbons to at least C_4. The tar yield is normally the residue left from solvent evaporation after filtering, and the BTX (benzene-toluene-xylene) fraction and the C_4 - C_8 fraction are often reported separately. In general, the tar amount reported includes volatile hydrocarbons where these are not given separately.

Saskatchewan (Estevan) Lignite

The tar and total volatiles yields given in Figure 2 for Lignite 3 show a maximum of about 10% maf at 650-700°C. Total volatiles are of the order expected for this lignite. Figure 3 shows the char yields for Lignite 3 also, and indicate a decrease in char obtained from 73% at 500°C to 59% at 750°C. This drop in char yield is accompanied by increases in gas yield and tar yield. The char from lignite was very reactive, and care was required in handling to prevent spontaneous combustion when fresh char was exposed to air, even at room temperature.

The yields of various gases are shown in Figure 4, and the hydrocarbon gas yields in Figure 5. A feature of lignite is the large yield of CO_2 and, at higher temperatures, of CO as well. A considerable amount of pyrolytic water was also formed. An estimate at 650°C indicates that about 61% of the original oxygen incorporated in the lignite is rejected as CO_2, CO or H_2O in pyrolysis.

Figures 6 and 7 give the results of elemental analyses for tars and chars from Lignite 3. The carbon content of the tars increases slightly with temperature while the hydrogen content decreases steadily. As a consequence, the H/C molar ratio in the tar decreases steadily with temperature, as shown in Figure 8. It would appear that better quality liquids are produced at lower temperatures, and hence some optimum condition involving quality vs. yields might exist for the liquid product. However, these liquids still contain a fair amount of oxygen (10-15%), and may therefore also contain small amounts of dissolved water which would slightly overstate the hydrogen content associated with hydrocarbons. Water content was not determined on these tars. However, it is believed that the water content, if any, would be small after solvent evaporation, probably less than 5%. The trend shown in Figure 8 is therefore a valid one even though it may contain some error.

The char shows an even stronger change in the H/C ratio as the temperature of pyrolysis increases, decreasing from a value of 0.53 at 500°C to 0.30 at 750°C. The hydrogen which is lost from the char, as well as the much smaller amount from the tar, appears as light hydrocarbon gases (see Fig. 5) or as BTX and C_4-C_8 fractions.

Forestburg Subbituminous Coal

A number of pyrolysis tests on Forestburg coal have been reported previously and only a limited number of additional tests were done in the present work. Product yields are plotted in Figures 9 to 12 for temperatures from 500°-700°C. Typical results from earlier work are included together with the results from the current study. Good agreement was obtained with work done a year earlier by others in our laboratory using essentially the same apparatus, as shown by the comparison of gas, tar and char yields in Figures 9 and 10, indicating a satisfactory degree of reproducibility in the pyrolysis tests. Good reproducibility is also indicated by the fact that tests were never done sequentially as a variable was changed, but were done in random order.

Tar yields of about 10.5% were obtained; very much the same as those from Lignite 3. Forestburg and the lignite coal have very similar elemental compositions, and very similar proximate analyses on an maf basis, although one is classed as a lower rank than the other. Indeed, there is a great similarity also in yields of other products from the two coals, with the Forestburg coal giving slightly higher tar and gas yields and slightly lower char yields, but with very similar trends. Again, high CO_2 and CO yields are obtained, and at the optimum temperature for liquid production of 650°C, some 80% of the oxygen in the coal has been rejected as CO_2, CO and H_2O. At higher temperatures, most of the oxygen in the coal is removed in this way.

Some elemental analyses of products is given in Table 6. As in the case of the Lignite 3 coal, the H/C ratio of both the tar and the char decreases with temperature, with the lost hydrogen appearing as light hydrocarbon gases.

Highvale (Wabumun) Subbituminous Coal

Again, because a number of pyrolysis tests for this coal have been reported, a limited number of tests were carried out. Results are shown plotted in Figures 13-16, together with some data from tests reported earlier (Scott et al., 1982). Results from the two sets of runs, performed some months apart by three different operators, show an acceptable degree of agreement.

Although the Highvale and Forestburg coal are quite similar in elemental composition, and both are classed as subbituminous coals, the Forestburg coal gives a significantly higher volatile matter yield than does the Highvale coal in a proximate analysis. Despite this fact, the Highvale coal gives a higher tar and BTX yield than does the Forestburg - about 11% liquid hydrocarbon vs 10%. Gas yield is lower and char yield significantly higher from the Highvale coal, although trends are very similar. As might be expected, the yields of all gas products are lower from the Highvale coal, but only slightly lower for all gases except CO_2, which is significantly lower. Apparently, the Forestburg coal contains more carboxylic acid groups, and therefore yields more CO_2.

Elemental analysis of the char and tars obtained at 650°C and 750°C shows the atomic H/C ratio to be about the same as that for tars from the Forestburg coal at the same temperatures. The same is also true of the H/C ratios of the chars. Again, these ratios show a significant decrease with temperature for both tars and chars.

An interesting comparison of tar yields is available because of work done at the Alberta Research Council on this coal, and additional results reported by them (Du Plessis, 1982). This comparison is shown in summary form in Table 3. The tar and light oil yield from any of the fast pyrolysis methods exceeds the yield in the Fischer or Gray-King assays by up to about 100%. This large yield of liquids over that predicted in the standard assay is common for many lower rank coals. It is not a universal characteristic, however, and because of this it is difficult to use the Fischer assay as a means of predicting the yield of pyrolytic liquid hydrocarbons.

Hat Creek Subbituminous Coal

Hat Creek coal was a very high-ash (46-48%), high-moisture content coal with a low-volatiles content. The results of pyrolysis tests over the range of 500°-700°C are shown in Table 4 on a maf basis. The maximum yield of liquid hydrocarbons was obtained at 650°C as for other low rank coals, but it amounted to only 5.5% maf (about 2.1% of the coal as fed). Gas yields were relatively high, significantly higher than the Lignite 3, Forestburg or Highvale coals, with very large amounts of CO_2 being generated, while yields of other gases were more comparable to those from other low-rank coals. It would appear that the Hat Creek coal is in some respects more similar to a lignite, although the Hat Creek coal has a much higher oxygen content (32% vs 22%) and gives a much lower char yield (ash free) than does the Saskatchewan lignite. Apparently, much of the oxygen is present as carboxylic acid groups which can be readily split off, but which do not yield any significant liquids. Water yield is also high from this coal, but it could not be quantitatively measured in these runs.

From elemental analysis, the H/C ratio of the tar appeared to show little change as pyrolysis temperature increased and had a value of 1.2 to 1.3. On the other hand, the H/C ratio for the char showed a steady decrease as temperature increased, with values very similar to those for other low-rank coals.

The very low yield of liquids and the very high ash content indicate that the Hat Creek coal is probably not a suitable feed for a pyrolysis process. However, it may be possible that some pre-treatment, such as ash removal, or acid washing, would increase tar yields.

Balmer Bituminous Coal

The Balmer coal is classed as a low-volatile bituminous caking coal with a low-oxygen content and a high-carbon content. Pyrolysis of Balmer bituminous coal was studied for temperatures from 500°-700°C, using the larger reactor which allowed more coal to be fed before reactor clogging was observed. Yields of major products are shown in Figure 17. The maximum tar yield occurred at 650°C and is quite clearly defined. A maximum in tar yield of 10.0 maf wt % was found, with BTX and light hydrocarbons accounting for an additional 1.4 maf wt % of coal fed. The sharp increase in tar yield in the 600° to 650°C range is accompanied by a sharp decline in char yield.

Yields of individual gases for the Balmer runs are shown in Figure 18. No H_2 was detected below 550°C and no CO below 600°C. The points on this graph may seem to be widely scattered but it should be noted that the entire vertical scale represents only 2% of maf coal fed, so any error will be magnified.

The outstanding feature of the low-volatile bituminous coal is the low gas yields, of which at least 50% are hydrocarbon gases, and the high char yields. The relatively larger (in terms of percentage of liquid product) amounts of BTX and C_4-C_8 hydrocarbons is also of interest. The original coal contains little oxygen (about 4%), and at optimal conditions about 50% of this is rejected as CO, CO_2 and H_2O. The resulting tars, therefore, should contain little oxygen. Elemental analysis of chars and tars shows that the H/C ratio for the tar is nearly constant at about 0.94 with temperature, in contrast to tars produced from lower rank coals, which have H/C ratios decreasing with temperature.

MacIntyre Bituminous Coal

Pyrolysis tests were carried out with this low-volatile bituminous caking coal at temperatures from 500°C to 675°C. The large reactor and a longer residence time of 0.8 seconds were used because of the agglomeration occurring in the sand and on the reactor walls during a run.

Product yields and individual gas yields for this coal are presented in Figures 19 and 20. Maximum tar and light hydrocarbon (C_4 to C_8) yields totalled 7.2 maf wt % at 675°C, which was the maximum temperature reached. It may be that the optimal temperature for maximum liquid yield is even higher than this value. The primary gas product was methane, showing a maximum yield of 1.9 maf wt % at 650°C. Gas yields were low, only about one half the liquid yields, while char represented 85-90% of the products.

Elemental analyses show that the H/C ratio for the MacIntyre char was nearly constant, as was also the case for the Balmer coal, with much the same value (0.57 and 0.60, respectively). The H/C ratio for the tars was also nearly constant at a value of about 0.9, only a little less than that for Balmer coal which was also nearly constant.

Devco Bituminous Coal

Five runs were performed using Devco coal covering the temperature range of 500°C to 700°C. All runs were in the large reactor with an N_2 atmosphere and a 0.8 second residence time, because of the highly caking nature of this coal, which had the highest free-swelling index of any of the coals tested (8.5).

Yields of gas, tar, C_4 to C_8 hydrocarbons, char, and gases are shown in Figure 21. A maximum tar yield of about 17% maf wt % appeared to occur at 650°C to 700°C. If the BTX and C_4 to C_8 yields are included with the tar, the yield becomes about 19% maf wt %. Yields of individual gases are shown in Figure 22.

From elemental analyses of products, the char H/C ratios showed a decrease as temperature increased, from 0.57 to 0.39, which is very similar to the values and behaviour shown by the lower rank coals. On the other hand, the H/C ratio for the tar was approximately constant as it was for other bituminous coals at 1.00 to 1.08, which is somewhat higher than the tar H/C ratios for MacIntyre or Balmer coals.

Considering the high yields of tar, the higher H/C ratio of the tar and its low-oxygen content, the Devco coal appears to be a very promising feed for a pyrolysis process for the production of liquid hydrocarbons. Further work is warranted with this coal or other high-volatile bituminous coals. This has also been the experience of Australian workers using high-volatile bituminous coals in a fluidized-bed reactor (Smith, 1981).

Sukunka Bituminous Coal

Three runs were carried out using Sukunka low-volatile bituminous coal from a sample supplied by the Energy Research Laboratories, CANMET. Table 5 shows the analyses of this coal with values taken from various sources. The variability of the ash content of this coal among the various analyses is interesting. However, on a dry ash-free basis, a reasonable agreement is obtained.

Table 6 gives the results of three pyrolysis tests, one at low temperature (533°C) and two near the temperature for maximum liquid yield from bituminous coals (650°C-700°C). Although the free-swelling index of this coal is given as 3.0, 4.5 and 7.0 depending on the sources, it was found to be one of the most difficult in our experience to feed and pyrolyze in a fluidized-bed. A high degree of agglomeration took place in both the sand bed and on the reactor walls; although some variations in procedure were tried, these met with little success. As a result the runs were difficult to complete, and a number of tests did not yield complete data. The values in Table 6 indicate a maximum tar yield of 12.16% with a 96.5% recovery at the highest temperature of 680°C. This yield is of the same order as that obtained from other low-volatile bituminous coals, e.g., Balmer, and agrees with that to be expected from the correlation for bituminous coals given by Smith (1981) which was developed at CSIRO.

The CSIRO correlation, which relates the tar yield at optimum conditions (600°C in the Australian work, but 650°C-700°C in our tests) to the H/C ratio of the coal, is reproduced as Figure 23. Shown on this plot are the maximum yields obtained in our tests from the four bituminous coals used. With the scatter of the correlations, the results from the present work agree well, although they are raw experimental points and have not been adjusted in any way.

Effect of Particle Size Variation

Pyrolysis tests in which particle size was varied were carried out for three coals - Saskatchewan lignite, Forestburg subbituminous and Balmer bituminous. Two standard feed sizes were used, −149 +74 μm (−100 +200 mesh) and −74 +44 μm (−200 + 325 mesh), so that the mean feed particle diameter varied by a factor of about 2. All runs were done at conditions close to those giving maximum liquid yield.

Table 7 shows the effect of changing particle size from −100 + 200 to −200 +325 mesh for Saskatchewan lignite and Forestburg subbituminous coals. For the lignite, gas yields decreased 5-6%, tar yields decreased 0.5-1.0% for the smaller particle size and char yields increased.

The Forestburg subbituminous coal showed a decrease in gas yield of 7-8% and a decrease in tar yield of 0.5-1.5% as particle size was reduced. The char yield increased by 10-12%.

The lower gas and tar yields and higher char yield are probably an effect of residence time. Although the residence time based on superficial gas velocities was the same for both particle sizes, it is expected that the actual residence times for the coal particles themselves were different. The lighter −200/+325 mesh particles would probably have a lower residence time than the larger −100/+200 mesh particles, inasmuch as a larger proportion would be easily swept from the reactor after some weight loss or attrition.

The effect of particle size on yields obtained from the Balmer coal showed that in this case also, the smaller particle size gave a lower gas yield, a lower tar yield and an increased char yield. These facts, together with the decreased yield of BTX, all indicate an insufficient residence time for the smaller solid particles, inasmuch as the apparent gas residence times were identical.

It is probable that an optimum particle size exists for each coal and for each type of reactor, such that heating of the particle and generation of volatiles is reasonably complete, but char does not accumulate unduly or remain for too long in the actual reaction zone. This size is probably most easily determined experimentally in each case.

In summary, the conditions for optimal pyrolysis yields will be a function of particle size and reactor type, as well as of other variables such as temperature and residence time. As a consequence, particle size must be treated as one of the basic variables of the pyrolysis system.

Effect of Residence Time

Residence times were varied for two coals, the Saskatchewan lignite and the Balmer bituminous coal. The nature of the fluid-bed reactor limits the range of gas residence times which can be used and still obtain satisfactory fluidization in a single reactor. In fact, to cover the maximum range of 0.2 to 1.4 seconds attained in these tests, two reactors, one larger than the other, had to be used as explained previously.

Residence time for Saskatchewan lignite - 100/ +200 mesh was varied from 0.2 to 1.4 seconds. The results of these runs are presented in Table 8. It can be seen that longer residence times produce more gas and less tar. The *residence time* used here is based on the net empty reactor volume divided by the inlet volumetric gas flow rate at reactor conditions. It is difficult to separate this gas residence time from the effect of char particle residence time. Included in Table 8 is data showing the percentage of the char remaining in the fluid-bed at the end of a run. It is possible that the presence of char particles remaining in the bed throughout the run may have some effect on product yields in addition to any effects caused by superficial gas residence time. However, if there is any such effect of char accumulation, the data given in Table 8 suggests it must be a minor influence.

It is clear from Table 8 that shorter residence times favour tar production. The results of Run 86 indicate that the optimal residence time for tar production may not be at the usual residence time of 0.45 seconds used in these studies. The results given in Table 8 are shown plotted in Figure 24, for the tar, and the tar + BTX. For the lignite coal, the shortest residence time of 0.2 seconds is clearly the best in terms of maximum liquid yield for the -149 $+74$ μm particle size used. The BTX fraction increases with longer heating time, and presumably more cracking, of the primary tar product, so that some of the loss of tar yield at longer times appears as incremental BTX product. However, about 15% of the tar is lost, mainly as additional gas product as reaction time increases from 0.2 to 1.4 seconds.

The results of residence variation with Balmer coal feed showed that over the range of 0.45 to 1.4 seconds, the highest yields of tar and of total hydrocarbon liquids were obtained at the shortest apparent gas residence time, although the residence time effect was less pronounced. Tar yield decreased by about 14% as residence time increased from 0.45 to 1.4 seconds. The only other clear trend was an increase in light hydrocarbon gases (C_1 to C_3) as residence time increased, apparently at the expense of tar product. Apparently, for both the lignite and bituminous coals, the minimum gas residence time is preferable, at least down to probably 0.2 seconds.

Tests with a Catalytic Fluid Bed

Tests were carried out using a hydrogenation-deoxygenation catalyst in the bed in place of the fluidizing sand. Fifteen grams of crushed Co-Mo-0401T (Harshaw Chemical Co.) sized to -60 $+100$ mesh were used as a fluid bed. The composition and properties of the catalyst are given below. The coals were tested in the catalytic reactor, both at 650°C, with a feed particle size of -100 $+200$ mesh. Apparent residence time was the standard 0.44 seconds, and a 100% hydrogen atmosphere was used. Composition of Harshaw Co-Mo-0402T Catalyst, ⅛" is as follows:

Co	3%
MoO_3	10%
SiO_2	6%
PABD	0.95 g/cc
Crush Strength	26 pounds

Because the hydrogen at 650°C reduces the catalyst readily, the catalyst was pre-reduced and the water formed measured. This amount was then used as a correction in the runs with coal.

Results for Hat Creek coal are shown in Table 9. This coal has a very high ash content (46.4% as fed). The yields obtained with sand in a nitrogen atmosphere and with the Co-Mo catalyst in a hydrogen atmosphere are compared. On a moisture and ash-free basis it is apparent that the catalyst has little effect on tar, gas or char yields. Material balances could not be completed because of difficulties with the water and ash balances. However, the composition of the product gas is interesting, because although the total gas yield is about the same, the amount of CO_2 is much less in the catalytic reactor and the CO much greater. However, the total carbon as ($CO + CO_2$) is essentially the same. The conclusion is that the catalyst is promoting the water gas shift reaction to reduce the CO_2 content and increase the CO and H_2O content. At 650°C, the equilibrium for this reaction somewhat favours CO and H_2O production. There is also a marked increase in CH_4 production, and some increase in C_2 and higher gaseous hydrocarbons.

Table 10 gives similar results for the Forestburg coal. In this case, because water resulting from catalyst reduction could be allowed for, a good material balance was obtained. Compared to yields in nitrogen with sand in the bed, the Co-Mo catalyst with a hydrogen atmosphere showed only minor differences in char or total gas yield. However, a drastic decrease in tar yield resulted to only one third that from the uncatalyzed reaction. A significant increase in BTX was obtained, but not of the same order as the decrease in tar yield. The amount of water produced from the catalyzed reaction increased significantly. This behaviour again supports the promotion of the water gas reaction by the catalyst as also shown by a corresponding increase in CO and a decrease in CO_2. Since the CO increase was greater than would be expected from either the incremental amounts of CO_2 disappearing or of H_2O formed, it is possible that the steam-methane reaction or the reaction of carbon with CO_2 was also catalyzed by the Co-Mo material. Methane yield and BTX yield were both increased by the catalyst as were the amounts of C_2 + saturated hydrocarbons.

In conclusion, the Co-Mo catalyst acted to decrease liquid yields, but did increase somewhat the yield of light hydrocarbons. This catalyst also significantly altered the product gas composition, but did not affect total yields of volatile gases to any large extent.

A comparison is given below of analyses for the tar product for runs with and without catalyst, both runs at 650°C, 0.44 seconds with Forestburg coal.

Tar Run 40	C = 74.54	H = 6.83	N = 1.9	O = 16.7	H/C = 1.10
Tar Run 132	C = 90.69	H = 6.56	N = 0.97	O = 1.8	H/C = 0.86

Although too much reliance should not be placed on elemental analyses of single samples, the above results suggest that the catalyst causes deoxygenation of the tar. In fact, for Run 132 the results in Table 10 indicate that 95% of the oxygen in the original coal is rejected as CO, CO_2 or H_2O. It appears, therefore, that the extreme reduction in tar yield is partially compensated by the removal of oxygen from the tar (from 16% to 2%), but a severe reduction in tar yield is still caused by the catalyst action. Other reaction conditions should be investigated to determine if better tar yields are possible, or better yields of C_2 + hydrocarbons, than obtained in Run 132, while at the same time the tar is substantially de-oxygenated.

CONCLUSIONS

A comparison of maximum liquid yields among Canadian coals of different ranks is shown in Table 11. The maximum hydrocarbon liquid yield (18.4% maf) is obtained from the eastern Canadian high-volatile Devco bituminous coal. There is apparently no general correlation between maf volatiles as determined by proximate analysis and tar yields by flash pyrolysis. However, it is interesting to observe that within the one rank of bituminous coals, the tar yields do increase as the maf volatiles increase. A similar trend does not appear to exist for low-rank coals.

As shown in Figure 23, the tar yield from Canadian bituminous (black) coals in flash pyrolysis is just about what would be expected from the CSIRO correlation, which was derived, in the main, for high-volatile bituminous coals. Again, it should be remembered that the data given in Table 11, and plotted in Figure 23, have not been adjusted or normalized in any way, but are the direct experimental values. A significant part of the material balance losses is probably due to loss of volatiles, and therefore the results given can be taken to be reasonably conservative.

In most cases, the effect of temperature on liquid yield was typical of the fluid-bed fast pyrolysis process. An optimum (maximum) yield was observed, usually at 600°-650°C. However, for two bituminous coals, this maximum yield occurred between 650°-700°C. The maximum point tends to be more pronounced for the bituminous coals and less so for the lower rank coals. The H/C atomic ratios of the tar product also show interesting variations with temperature. For all the low-rank coals, the H/C ratio of the tar decreases with temperature from about 1.25 to 0.9 over the range of 500°-750°C. However, for the higher rank coals the H/C ratio of the tar is reasonably constant at 0.90 to 1.05 with the lower values corresponding to the lower volatile bituminous coals. The approximate oxygen content does not show any very clear trends with temperature, and varies from 8-16% for low-rank coals and 8-10% for higher rank coals. Although the oxygen content of the raw coals varies widely, the deoxygenation during pyrolysis by the formation of CO, CO_2 and H_2O appears to be much more effective for the low-rank coals than it is for bituminous coals.

The H/C atomic ratio of the chars show much the same pattern of behaviour with temperature as do the tars. The H/C ratio in chars for lower rank coals decreases steadily with temperature from about 0.6-0.35 over the range of 500°-750°C. However, the H/C ratio of the chars for the bituminous coals remains reasonably constant at 0.55 to 0.65 except for Devco coal which shows a small decrease with temperature (from 0.57 to 0.39). The H/C ratio indicates to some degree the nature of the material. The tars with H/C ratios of unity or slightly greater, suggest primarily simple single aromatic ring compounds, with more ring substituents, such as cresols, xylenes or phenols, etc., for the lower rank coals and fewer for the higher rank coals. The H/C ratios of the order of 0.5 found in the chars suggest polynuclear aromatic structures containing several ring units.

Residence time cannot be varied readily over wide ranges in a fluidized-bed reactor, and two sizes of reactor were required in this work to obtain the range 0.2-1.4 seconds. The residence time effect was investigated in detail for only one low-rank coal and one bituminous coal. The shortest time (0.2 or 0.45 seconds, respectively) gave the highest tar yields, with the effect being more pronounced with the lower rank coal. However, it should be remembered that the use of very short residence times in fluidized beds requires some further basic investigations to develop adequate reactor scale-up information.

The use of a deoxygenation-hydrogenation catalyst (Co-Mo) in place of sand as the fluidized solid with a hydrogen atmosphere in the reactor did not appear to affect product yields for a low-rank coal (Hat Creek), but did affect product gas composition, apparently by catalysis of the water gas reaction. For another low-rank coal (Forestburg) the catalyst reduced tar yields sharply, and although the tar formed was low in oxygen, this accounted for only a minor part of the yield loss. The product gas again had a composition indicating catalysis of gas phase reactions. It would appear that, at least at atmospheric pressure, this particular catalyst did not have any really beneficial effects during pyrolysis. However, the fact that significant effects were observed, even if not all desirable as in this case, suggests that further investigations with different catalytic materials might yield useful and beneficial results which could offer alternative reaction schemes.

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TABLES

Table 1 – Proximate analyses

Type	Ash	Moisture	FC	VM	FC	VM	Oil yield Fischer	FSI
	%	%	%	%	maf %	maf %	maf (3) %	%
Estevan Lignite I (2)	8.25	28.4	34.75	28.61	54.85	45.15	–	0
Estevan Lignite 3 (1)	6.29	7.93	42.67	43.11	49.74	50.26	–	
Forestburg (1)	6.5	10.0	41.96	41.31	50.25	49.47	–	0
Highvale (1)	10.7	17.3	44.50	29.17	61.80	40.51	5.9	0
Hat Creek (1)	50.7	4.0	14.8	30.5	32.67	67.33	–	0
MacIntyre (2)	7.47	0.79	74.24	17.50	80.92	19.08	3.7	4.5
Balmer (2)	9.78	0.64	69.71	19.87	77.82	22.18	6.4	4.0
Sukunka (1)	9.00	1.88	69.9	21.1	78.4	23.7	5.2	3.7
Devco (1)	2.9	1.2	60.96	34.98	63.56	36.47	14.2	8.5

(1) Analysis by Coal Research Laboratory, University of Waterloo
(2) Analysis by Energy Research Laboratory, CANMET
(3) Furimsky et al. (1981)

Table 2 – Ultimate analyses
maf basis

Type	C%	H%	S%	N%	0 % (by difference)	H/C
Sask. Lignite I (2)	70.82	4.75	0.64	1.28	22.51	.80
Sask. Lignite 3 (1)	71.2	4.24	N.D.	1.64	22.9	.71
Forestburg (1)	71.2	4.50	0.60	1.53	22.2	.76
Highvale (1)	75.4	4.1	0.2	1.10	19.3	.65
Hat Creek (1)	60.36	2.8	N.D.	1.54	32.7	.56
MacIntyre (2)	93.13	4.66	0.46	1.30	0.46	.60
(1)	88.68	4.4	N.D.	1.2	5.7	.60
Balmer (2)	90.36	4.79	0.30	1.26	3.29	.64
(1)	89.08	4.28	N.D.	1.45	5.19	.58
Sukunka (2)	86.2	4.53	0.69	1.75	3.1	.63
Devco (2)	87.14	5.50	1.09	1.73	4.54	.76
(1)	86.33	5.48	N.D.	1.82	5.28	.76

(1) Analyses by Coal Research Laboratory, University of Waterloo
(2) Analyses by Energy Research Laboratories, CANMET

Table 3 – Pyrolysis of Wabamun (Highvale coal) – comparison of yields by various methods

Method	Products (wt % maf coal)				
	Char	Tar & Light Oil	Water	Gas	Total
Fischer-Schrader[3] (550°C, 1.5 hr)	72.6	5.9	10.9	10.6	100
Fluid-Bed[4] (550°C, 0.44 sec)	78.2	7.3	[5]	10.7	96.2[6]
Gray-King[3] (600°C, 1 hr)	69.5	6.6	7.9	16.0	100
Fluid-Bed[4] (600°C, 0.44 sec)	74.9	12.2	[5]	13.5	100.5[7]
FTIR Vacuum[3] (650°C, 10 sec)	66.7	15.0[1]	11.4	6.9	100
Occidental Flash[3] (650°C, 2 sec)	64.0	14.2[2]	2.7	19.1	100
Fluid-Bed[4] (650°C, 0.44 sec)	69.1	10.4	4.2	15.8	99.5[8]
	66.5	11.2	2.7	14.1	94.4[9]
ASTM Proximate Analysis (950°C, 7 min)	60.4	39.6			100

(1) Light oil estimate by difference
(2) Light oil is included partly in gas and partly in tar
(3) Reported in "Coal Conversion Research Program at the Alberta Research Council" by M.P. DuPlessis, Journal of Canadian Petroleum Technology, July-August, 1982, pp. 79-88
(4) Experiments performed at UW
(5) Not reported
(6) Run 51
(7) Run 44
(8) Run 47
(9) Run 22

Table 4 – Pyrolysis of Hat Creek −149 +74 μm

		15.4% moisture, 46.4% ash 0.45 sec. residence time, N_2 atm				
Temp (°C)		500	550	600	650	700
Run #		129	130	128	127	126
Yield (maf wt %)	H_2	–	0.2	0.3	0.4	0.7
	CO	2.6	3.0	4.1	4.7	6.1
	CO_2	10.5	10.2	13.5	13.4	18.6
	CH_4	0.4	0.6	0.7	1.0	1.2
	C_2H_4	0.1	0.2	0.2	0.3	0.5
	C_2H_6	0.1	0.2	0.1	0.1	0.2
	C_3	0.2	0.2	0.2	0.3	0.4
	Gas	14.1	14.5	19.2	20.0	27.0
	Tar	2.6	3.1	3.0	4.5	3.2
	BTX	0.2	0.2	0.4	0.2	0.2
	$C_4 \rightarrow C_8$	1.0	0.7	0.8	0.8	0.9
	LHC[1]	3.8	4.0	4.2	5.5	4.3
	CHAR	56.9	56.3	51.8	49.2	39.7
	H_2O	–	–	–	–	–
Total		74.8	74.7	75.2	74.7	71.1

(1) LHC = light hydrocarbons = Tar + BTX + $C_4 \rightarrow C_8$

Table 5 – Properties of Sukunka coal

	Proximate Analysis, %					
	Moisture	Volatiles		Fixed Carbon		Ash
	As is	As is	DAF	As is	DAF	As is
Furimsky*	1.90	24.0	25.3	70.7	74.5	3.2
UBC**	1.08	20.6	24.0	65.14	76.0	13.18
Waterloo	1.88	21.1	23.7	69.9	78.4	9.00
EMR***	1.79	21.15	25.7	61.68	74.3	15.98

Ultimate Analysis, DAF basis

	C	H	S	N	O	H/C
Furimsky	88.51	4.95	0.53	1.37	4.6	0.67
UBC	89.98	4.53	0.69	1.75	3.1	0.60
EMR	86.2	4.71	0.68	1.58	4.4	0.66
Waterloo	89.69	4.55	N.D.	1.84	3.9	0.61

* *E. Furimsky, R. Belanger and J. Jorgensen, "The Pyrolysis of Canadian Coals for the Production of Fuels and Petrochemicals", Workshop on Pyrolysis, Fredericton, Jan. 5th, 1981*

** *Ph.D. thesis of Al. Jarallah, Dept. of Chemical Engineering, University of British Columbia, 1983*

*** *EMR Energy Research Laboratories, CANMET, Ottawa, Analysis of Jan. 1984, of sample supplied by M. Skubnik*

Table 6 – Product yield, Sukunka coal

	Ash 9.00%, Moisture 1.88%, N_2 atmos.		
Run	143	146	145
Temperature °C	533	666	680
Particle size, µm	−595 + 250	−1195 + 595	−595 + 250
Approx. Vapour Residence Time, sec.	0.50	0.35	0.50
Yields, % by weight, maf			
Gases	3.30	4.51	5.70
Tar	4.81	8.84	13.64
Water	0.0	N.D.	N.D.
Char	92.85	77.39	78.78
Total Recovery	100.96	90.74	98.12
Gas Yields, % by weight, maf			
H_2	0.10	0.22	0.30
CO	0.29	0.46	0.73
CO_2	1.37	0.85	0.93
CH_4	0.92	1.93	2.55
C_2H_4	0.08	0.17	0.22
C_2H_6	0.24	0.38	0.45
C_3's	0.18	0.22	0.29
C_4+	0.16	0.21	0.22

Table 7 – Effect of particle size

N_2 atm, type 1 reactor
0.45 sec residence time

Run		61	68	66	69	46	40	75
Coal		SASK LIG	SASK LIG	SASK LIG	SASK LIG	FOREST	FOREST	FOREST
Moisture (%)		7.0	7.0	7.0	7.0	9.2	9.2	9.6
Ash (%)		9.1	9.1	9.1	9.1	6.7	6.7	6.5
Temp. (°C)		650	650	600	600	650	650	650
Mesh Size		− 100 + 200	− 200 + 325	− 100 + 200	− 200 + 325	− 100 + 200	− 100 + 200	− 200 + 325
Yield (maf wt %)	Gas	13.9	9.1	13.8	7.6	17.6	16.6	9.4
	Tar	9.4	8.5	8.4	7.8	9.5	8.5	8.0
	Char	61.9	75.3	67.8	82.6	58.5	64.3	73.9
	BTX	0.4	0.2	0.4	0.1	0.3	0.4	0.2
	H_2O	9.2	9.3	8.3	9.9	–	–	1.5
	Total	94.8	102.4	98.7	108.0	85.9	89.8	93.0

Table 8 – Effect of residence time at 650°C

Saskatchewan Lignite – 149 + 74 µm
N_2 atm, 7.6% moisture, 8.8% Ash

		Large Reactor			Small Reactor	
Run		81	82	84	91	86
Residence Time (sec)		1.4	0.8	0.45	0.45	0.2
Yields (maf wt %)	Gas	20.0	16.7	14.6	19.0	15.6
	Tar	7.2	7.7	8.4	8.1	9.1
	Char	61.3	64.3	63.7	64.1	66.8
	BTX	0.7	0.9	0.5	0.5	0.3
	H_2O	4.8[1]	4.6[1]	4.6[1]	5.9	6.6[2]
	$C_4 \rightarrow C_8$	1.8	– [3]	1.9	1.8	1.6
	Total	95.9	94.0	93.5	99.4	100
Total Orig. Liq. (maf wt %)		9.7	10.2[4]	10.8	10.4	11.0
% of Char in Bed		39.6	2.7	1.2	30.9	0

(1) – estimated
(2) – by difference
(3) – not determined
(4) – excluding $C_4 \rightarrow C_8$

Table 9 – Tests with CoMo-0401 T catalyst and Hat Creek coal

Catalyst 15 grams −250 +149 µm
Coal feed −149 +74 µm Hat Creek coal, 15.4% H_2O, 46.4% ash as fed
Reactor – type 1, 650°C, 1 atm abs. H_2, 0.44 secs.
Yields, mass %

	Nitrogen + Sand		Hydrogen + CoMo-0401	
	Run 127		Run 131	
	As fed	maf	As fed	maf
Char	65.22	49.26	62.67	42.59
Tar	1.70	4.45	1.54	4.03
Gas	7.65	20.04	7.60	19.90
H_2	0.153	0.40	–	–
CO	1.78	4.65	4.40	11.51
CO_2	5.11	13.37	1.83	4.79
CH_4	0.37	0.96	0.98	2.57
C_2H_4	0.099	0.26	0.07	0.18
C_2H_6	0.051	0.13	0.14	0.38
C_3	0.113	0.30	0.17	0.44

Table 10 – Tests with CoMo-0401 T catalyst and Forestburg coal

Catalyst 15 grams −250 +149 µm
Coal feed −149 +74 µm Forestburg subbituminous
10.0% moisture, 6.73% ash as fed
C 71.2% H 4.5% maf
Reactor – Type 1, 650°C, 1 atm abs. H_2, 0.44 secs.
Yields, mass %

	Nitrogen + Sand		Hydrogen + CoMo-0401	
	Run 16		Run 132	
	As fed	maf	As fed	maf
Char	56.12	59.31	57.02	60.39
Tar	8.74	10.50	2.58	3.10
BTX	0.24	0.29	1.06	1.27
Water	17.10	8.53	20.01	12.02
Gas	15.62	18.76	17.93	21.53
Total	97.82	97.39	98.60	98.31
H_2	0.30	0.36		
CO	4.37	5.25	8.86	10.64
CO_2	9.51	11.42	5.02	6.03
CH_4	1.00	1.19	2.76	3.31
C_2H_4	0.25	0.30	0.23	0.28
C_2H_6	0.20	0.24	0.43	0.51
C_3			0.39	0.47
C_4			0.24	0.29

Table 11 – Maximum liquid yields

	Estevan Lignite	Forestburg Subbit.	Highvale Subbit.	Hat Creek Subbit.	Devco hvA*	MacIntyre Bit.	Balmer Bit.	Sukunka Bit/ Subbit.	Estevan Lignite Acid-Washed
Temp. (°C)	650	650	650	650	650	675	650	680	600
Res. Time, s	0.45	0.45	0.45	0.45	0.80	0.80	0.80	0.50	0.45
Yields wt % maf, at optimum liquid yield									
Gas	14.3	17.9	15.8	20.0	4.4	3.7	3.9	5.7	17.0
Max.Tar**	9.9	9.7	10.7	5.3	17.8	7.0	11.0	13.6	13.7
Char	62.8	58.5	69.1	49.2	67.8	86.9	80.7	78.8	56.0
BTX	0.43	0.4	0.44	0.2	0.6	0.2	0.4	–	0.1
H_2O	6.9	7.0	3.9	–	4.7	3.8	1.9	–	5.9
Total	94.3	93.5	99.9	74.7	95.3	101.6	97.9	98.1	92.7
Tar Atomic H/C	1.14	1.10	1.06	1.22	1.08	0.91	0.92	–	0.86

* *Average of two runs*

** *Tar includes $C_4 \rightarrow C_8$ fraction*

FIGURES

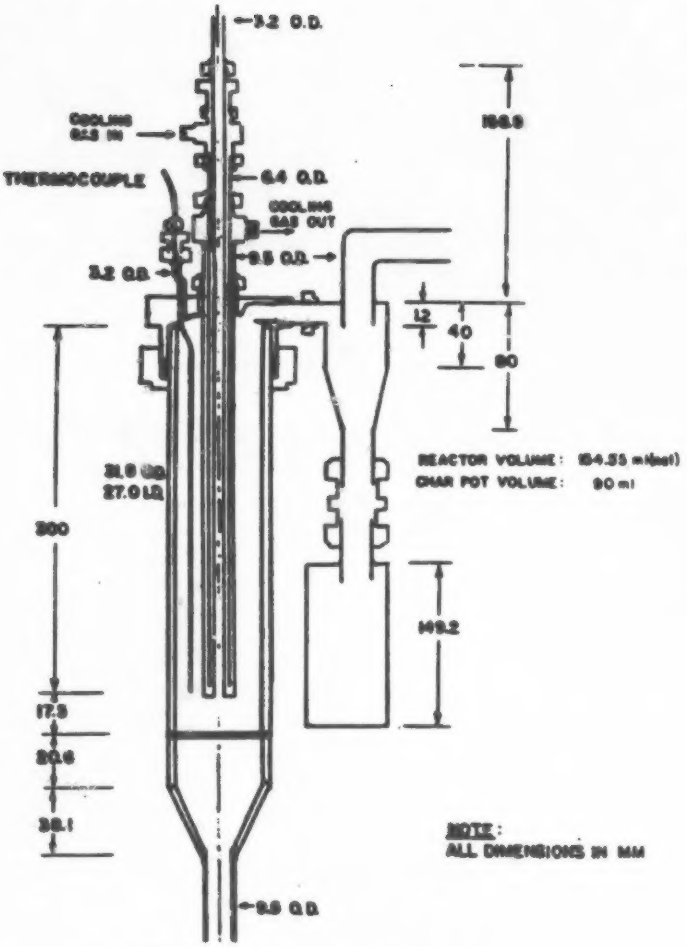
3.2 O.D.
COOLING GAS IN
THERMOCOUPLE
6.4 O.D.
COOLING GAS OUT
9.5 O.D.
3.2 O.D.
168.9
12
40
80
31.8 O.D.
27.0 I.D.
300
REACTOR VOLUME: 154.55 ml(bed)
CHAR POT VOLUME: 90 ml
149.2
17.5
20.6
38.1
NOTE:
ALL DIMENSIONS IN MM
9.5 O.D.

Fig. 1 – Details of large fluid-bed reactor

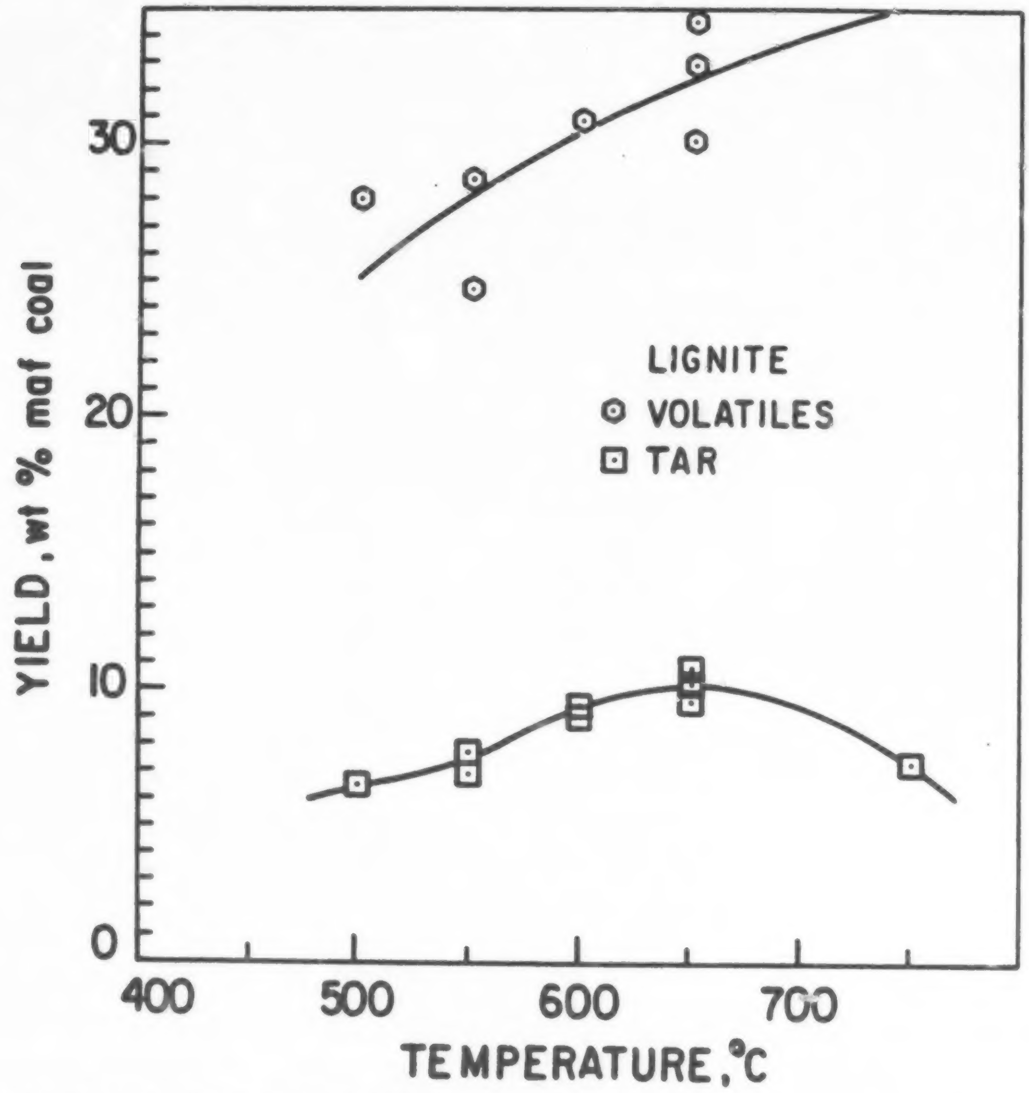

Fig. 2 – Tar and Volatiles Yield from Saskatchewan (Estevan) Lignite 3, -149 +74 μm, N_2, 0.45 S.

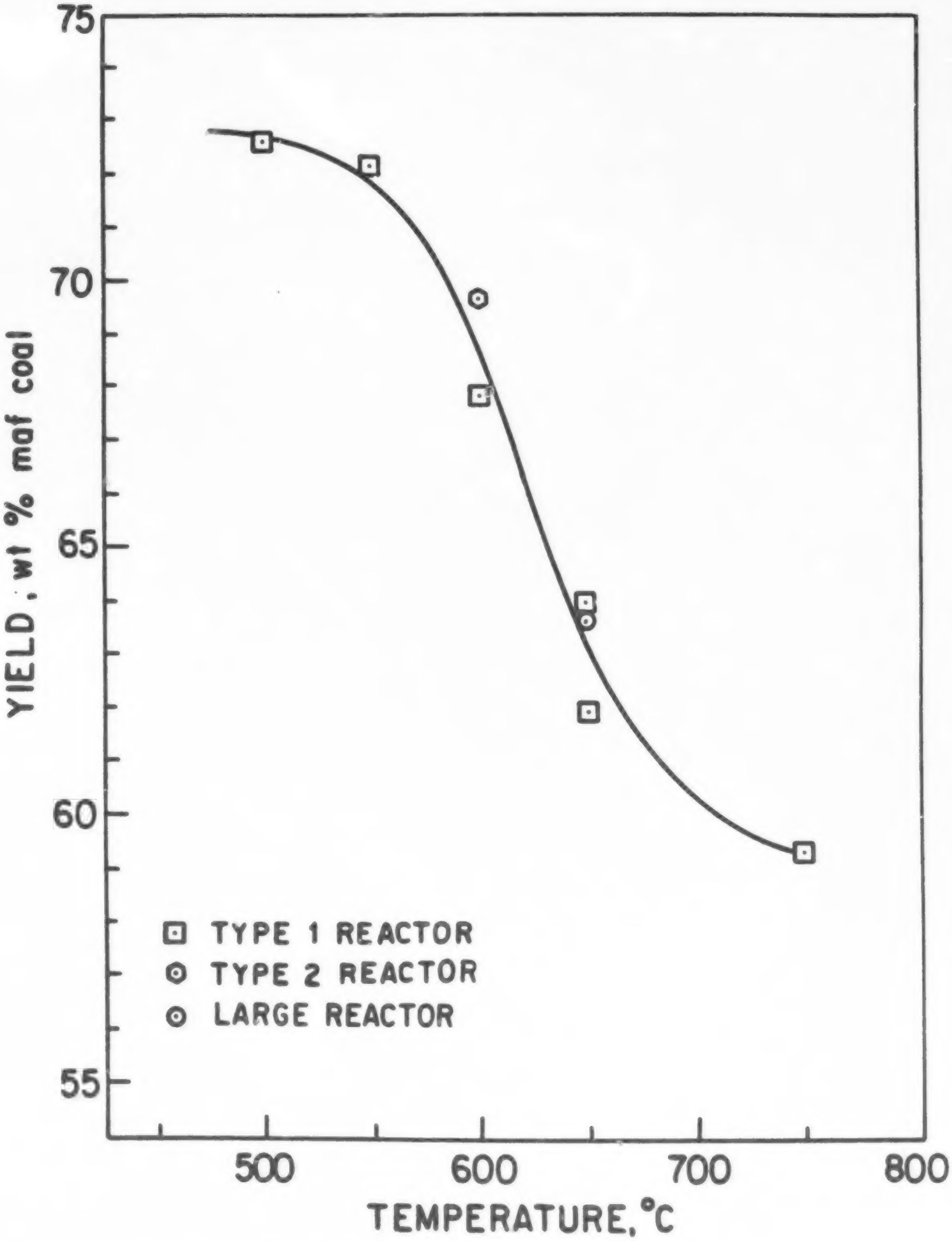

Fig. 3 – Char Yields, Sask. Lignite 3, -149 +74 μm, N_2, 0.45 S.

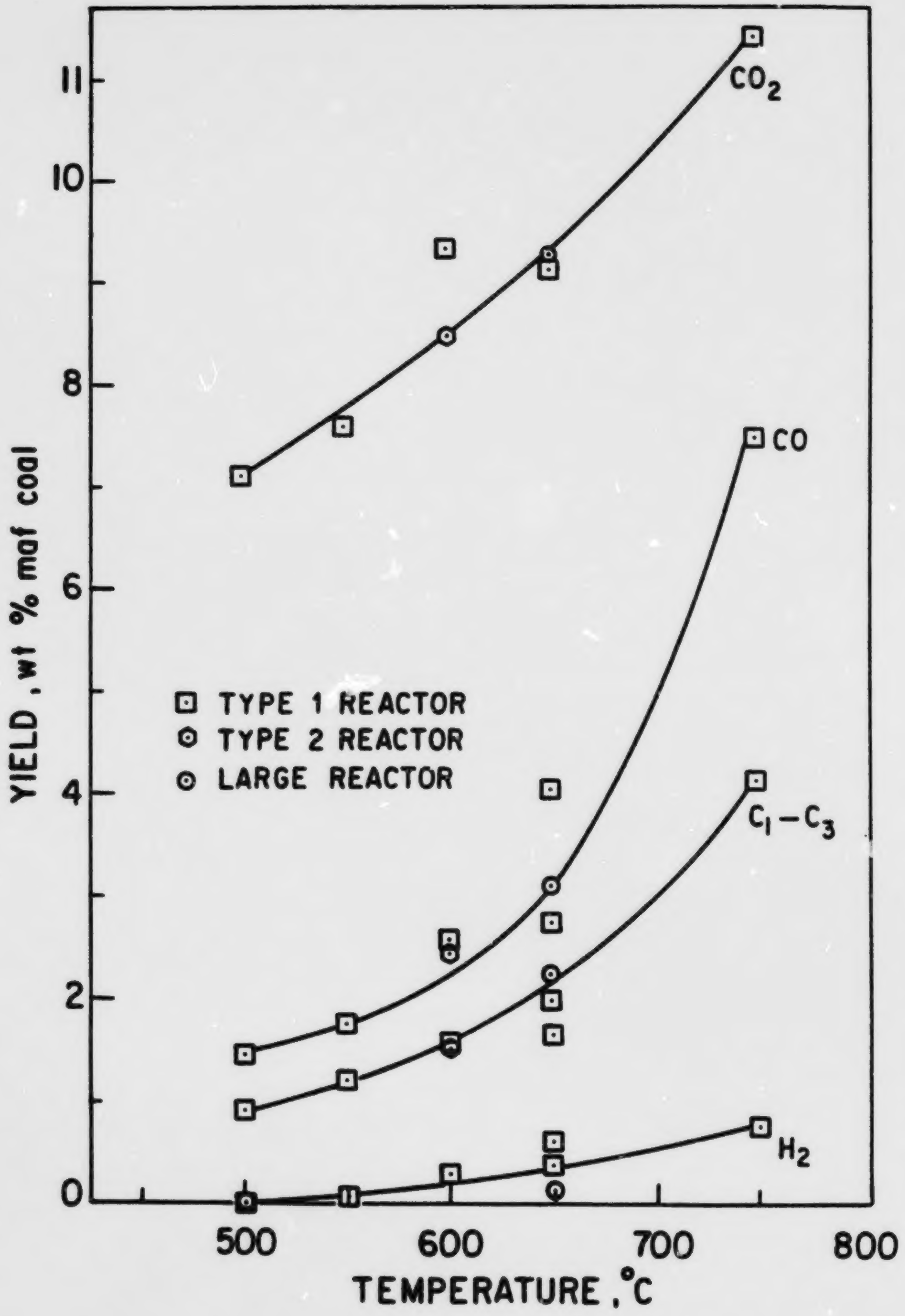

Fig. 4 – Gas Component Yields, Sask. Lignite 3, -149 +74 μm, N_2, 0.45 S.

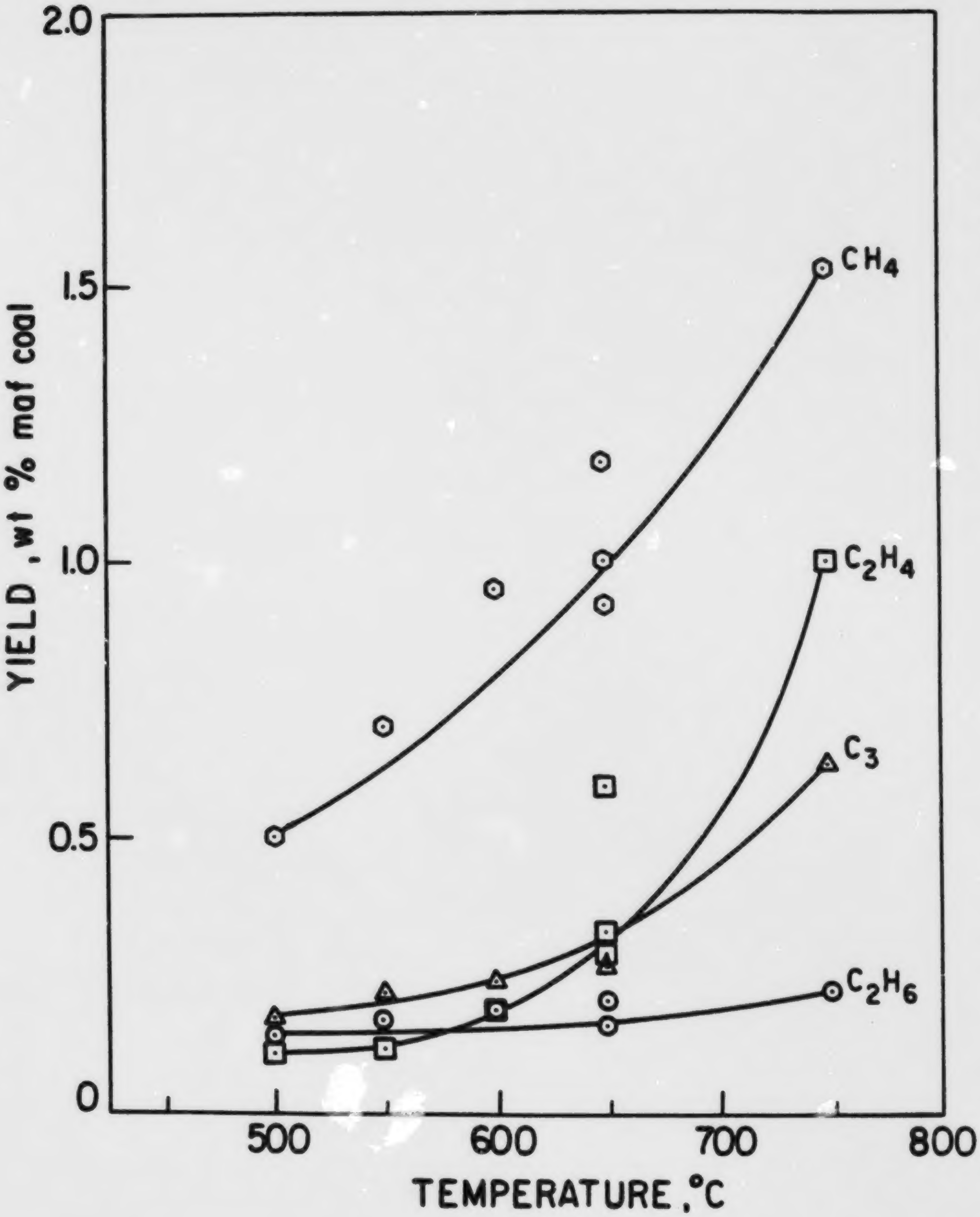

Fig. 5 – Hydrocarbon Gas Yields, Sask. Lignite 3, -149 +74 μm, N_2, 0.45 S.

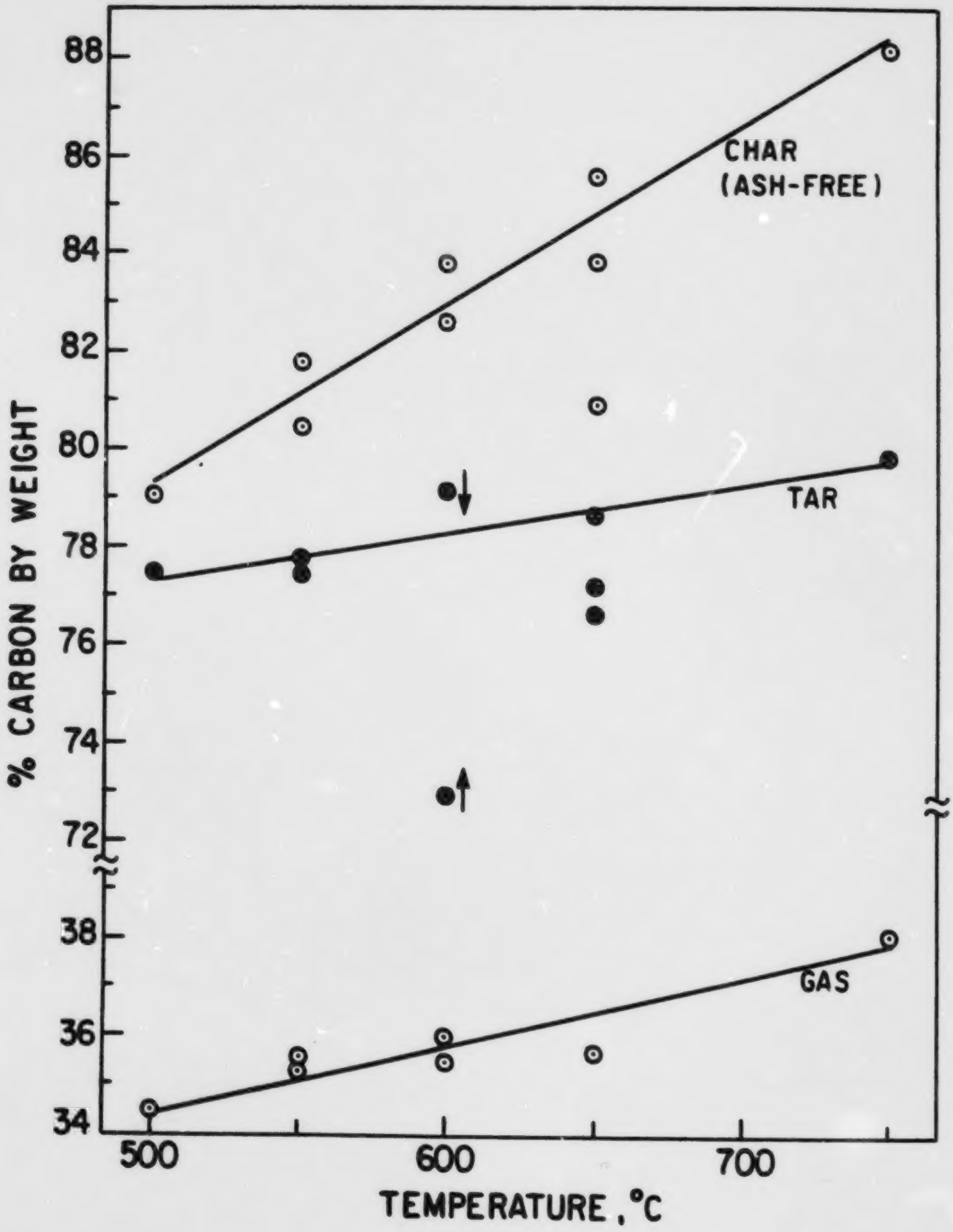

Fig. 6 – Carbon Analyses of Products, Sask. Lignite 3, -149 +74 μm, N_2, 0.45 S.

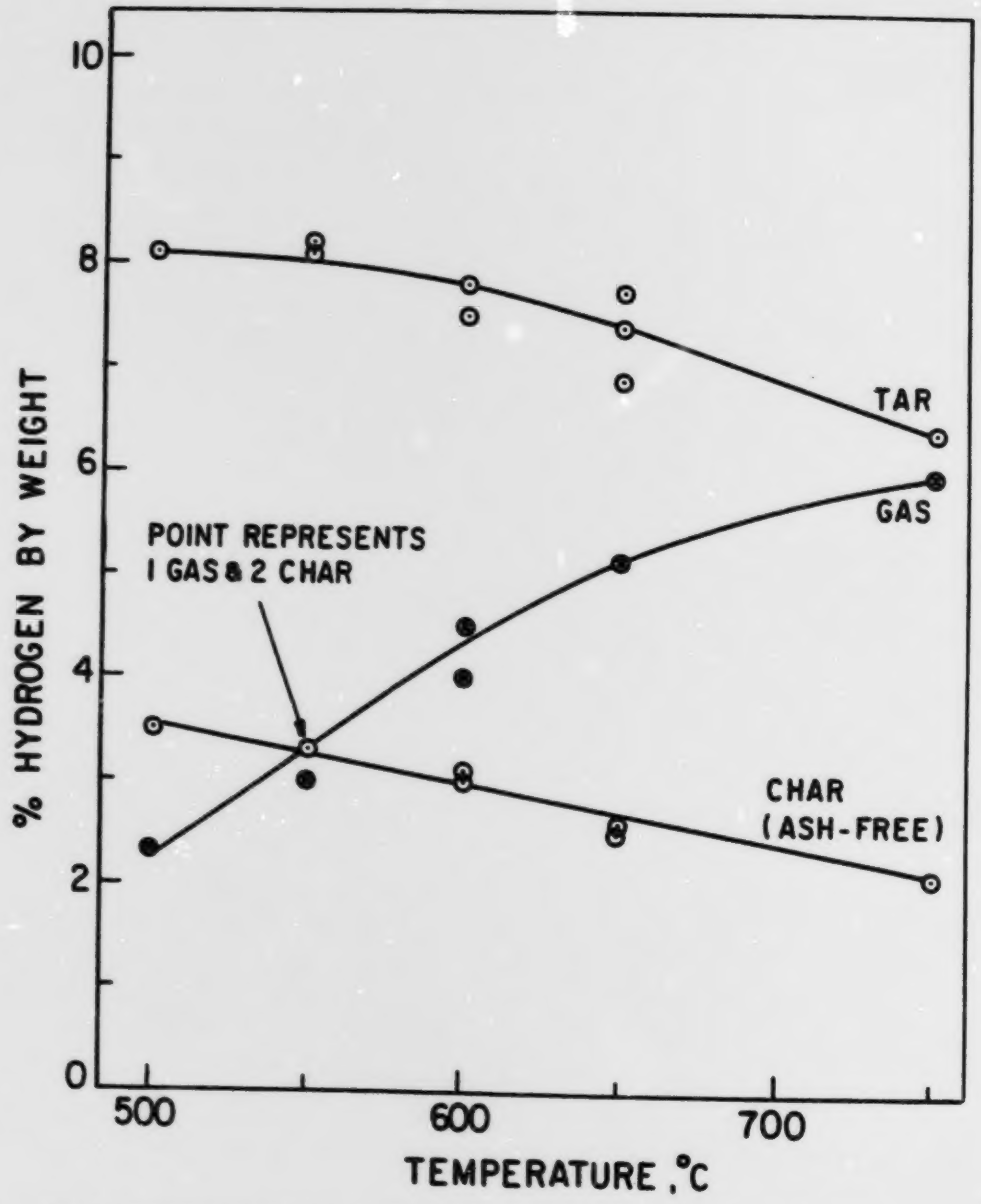

Fig. 7 – Hydrocarbon Analyses of Products, Sask. Lignite 3, -149 +74 μm, N_2, 0.45 S.

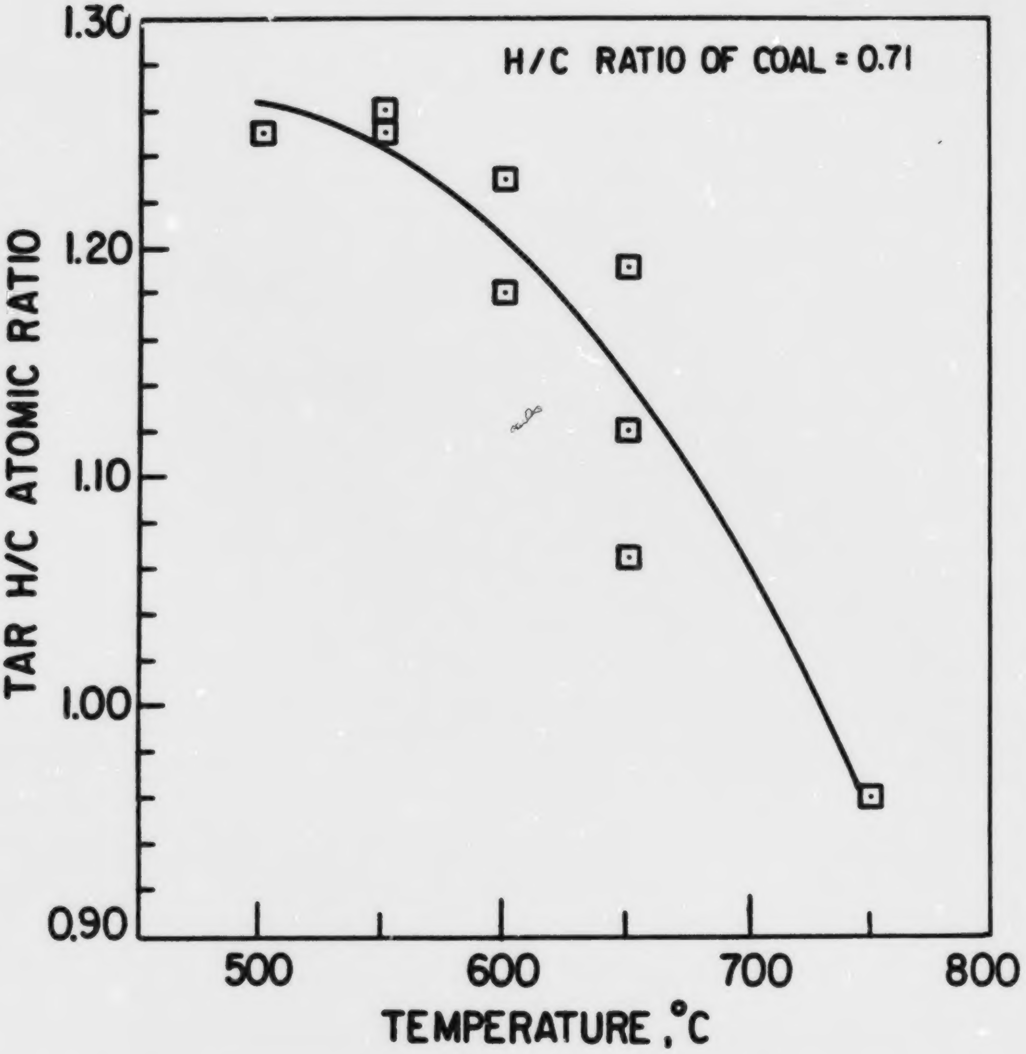

Fig. 8 – Atomic H/C Ratio of Tars as a Function of Temperature, Sask. Lignite 3, -149 +74 µm, N_2, 0.45 S.

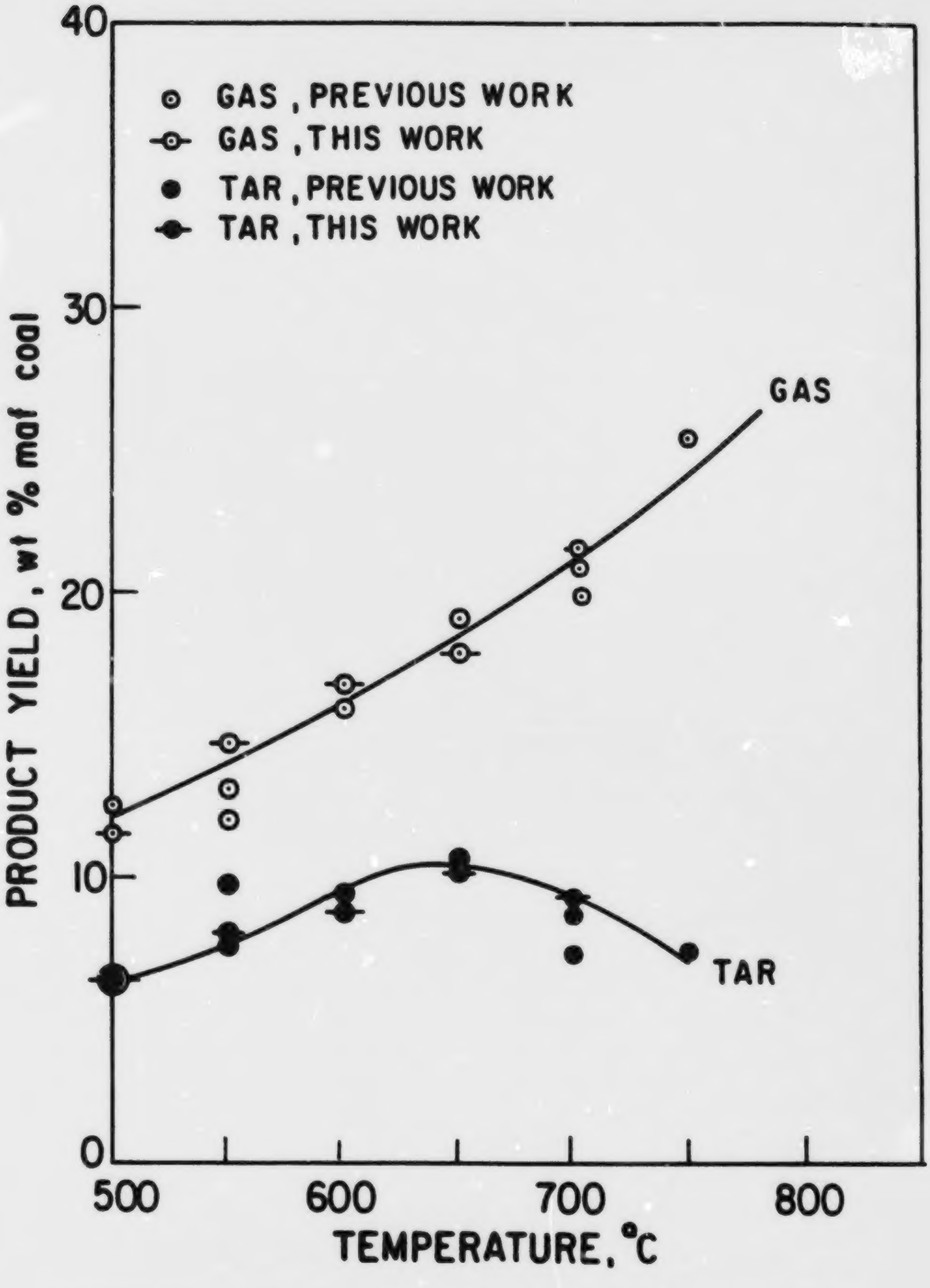

Fig. 9 – Gas and Tar Yields, Forestburg Subbituminous, -149 + 74 µm, N_2, 0.44 S.

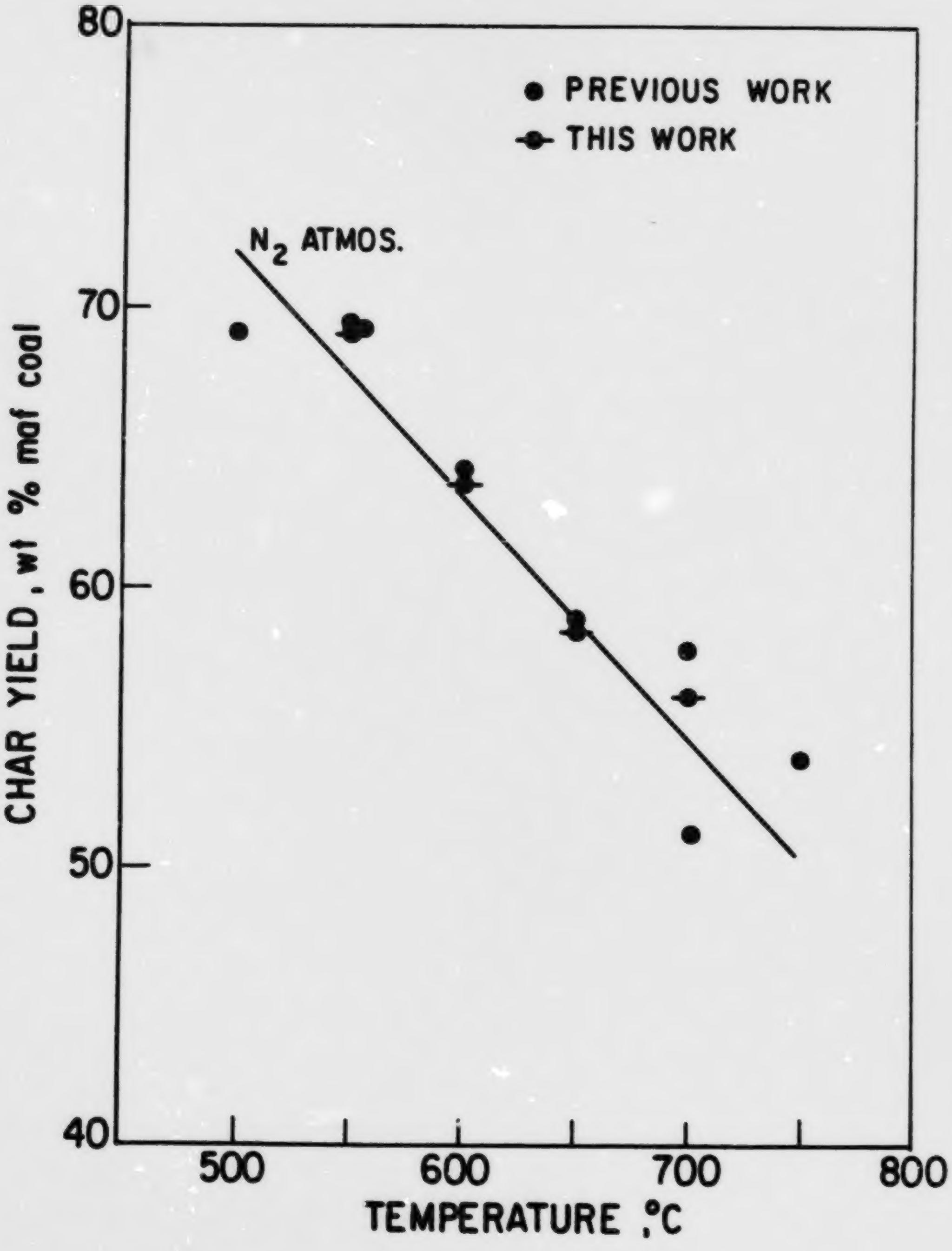

Fig. 10 – Char Yield, Forestburg Subbituminous, -149 +74 μm, N_2, 0.44 S.

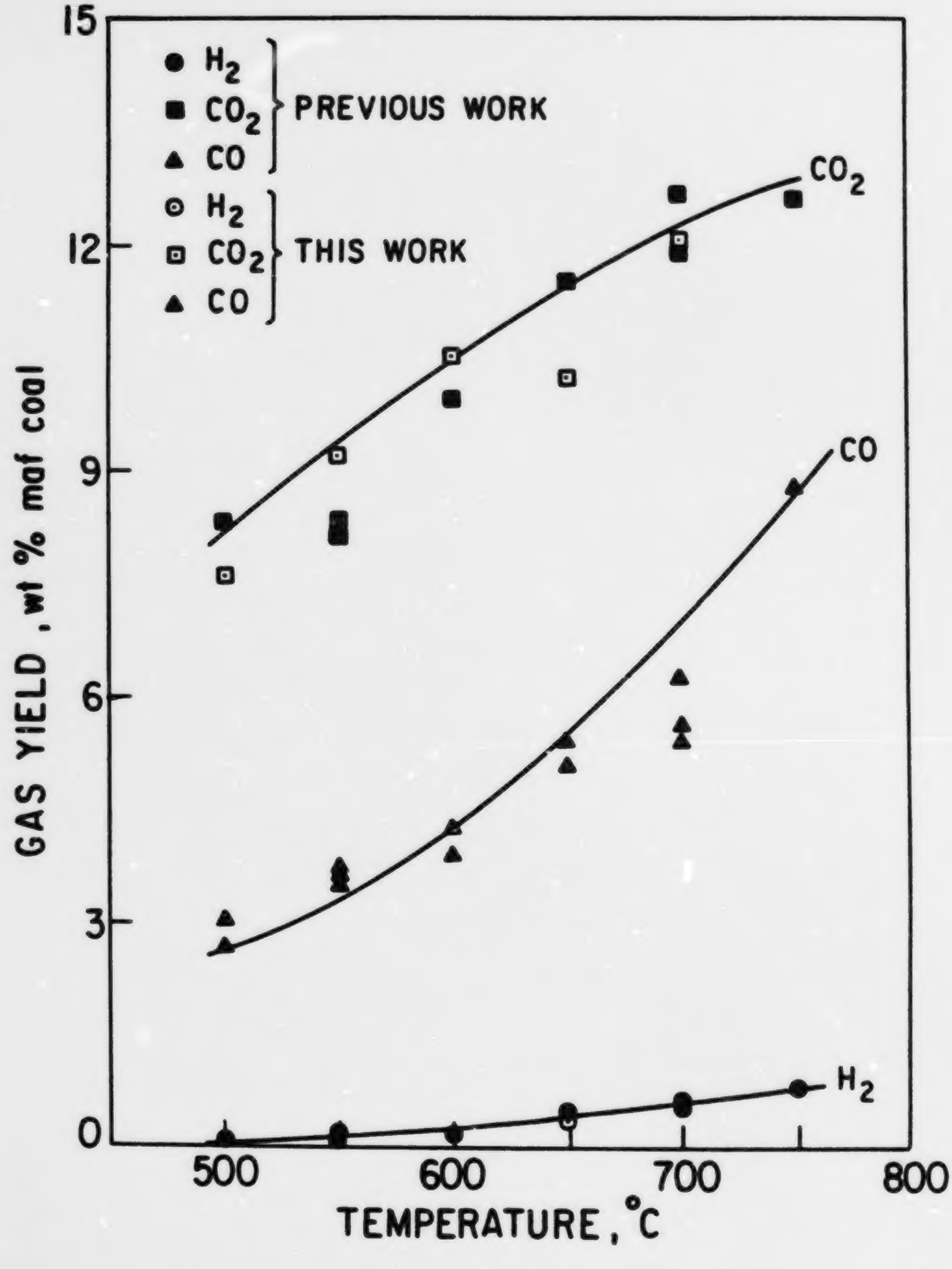

Fig. 11 – Gas Component Yields, Forestburg Subbituminous, -149 + 74 μm, N_2, 0.44 S.

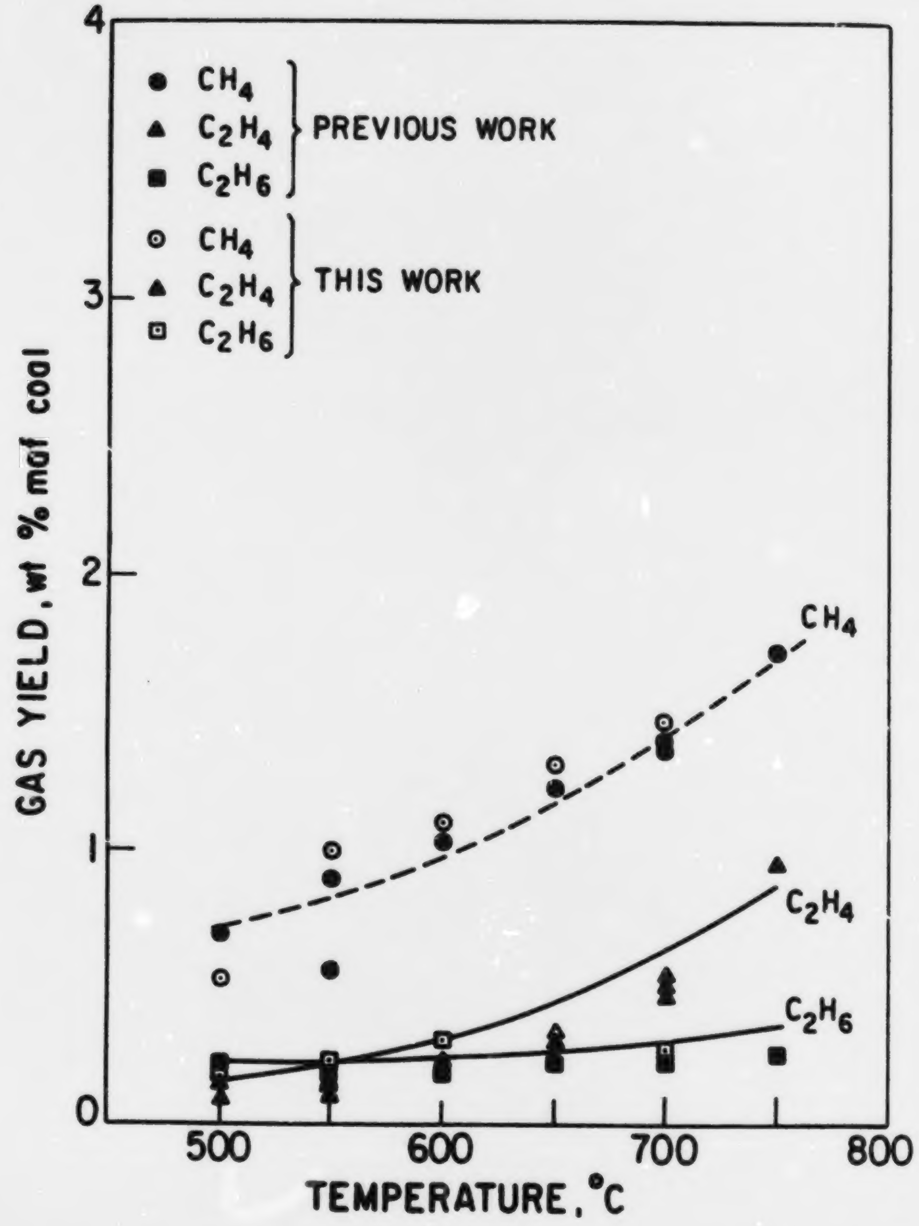

Fig. 12 – Hydrocarbon Gas Yields, Forestburg Subbituminous, -149 +74 µm, N_2, 0.44 S.

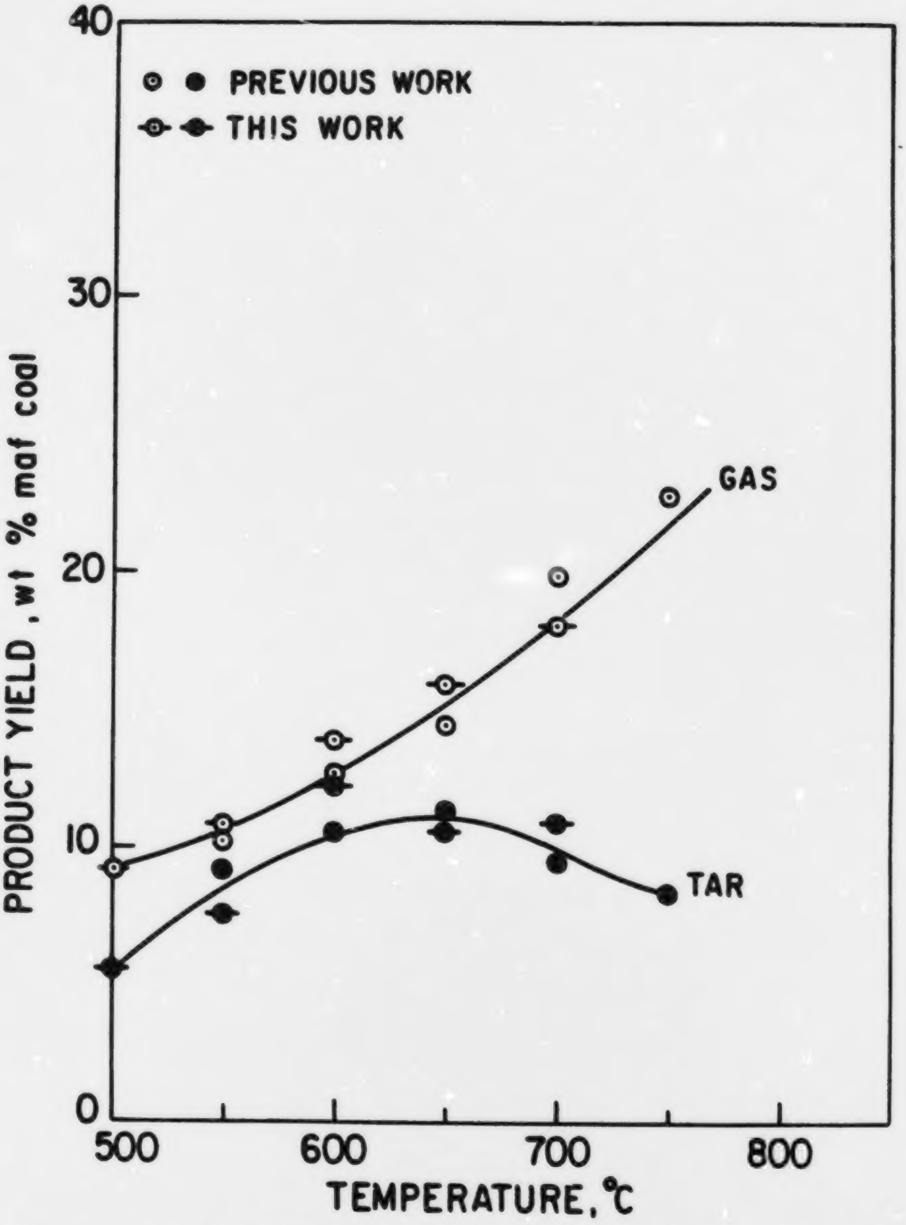

Fig. 13 – Gas and Tar Yields, Highvale Subbituminous, -149 + 74 μm, N_2, 0.44 S.

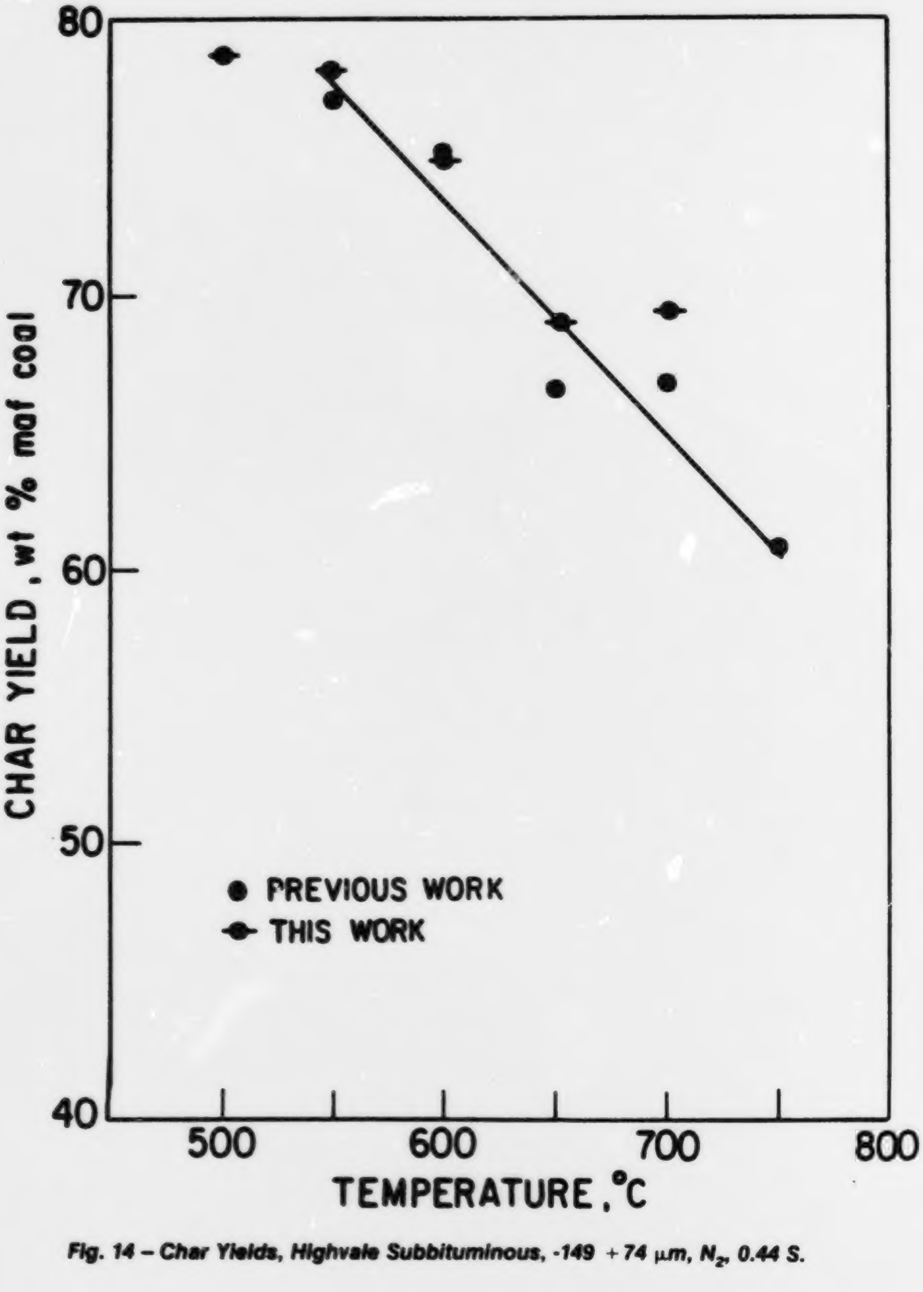

Fig. 14 – Char Yields, Highvale Subbituminous, -149 +74 μm, N_2, 0.44 S.

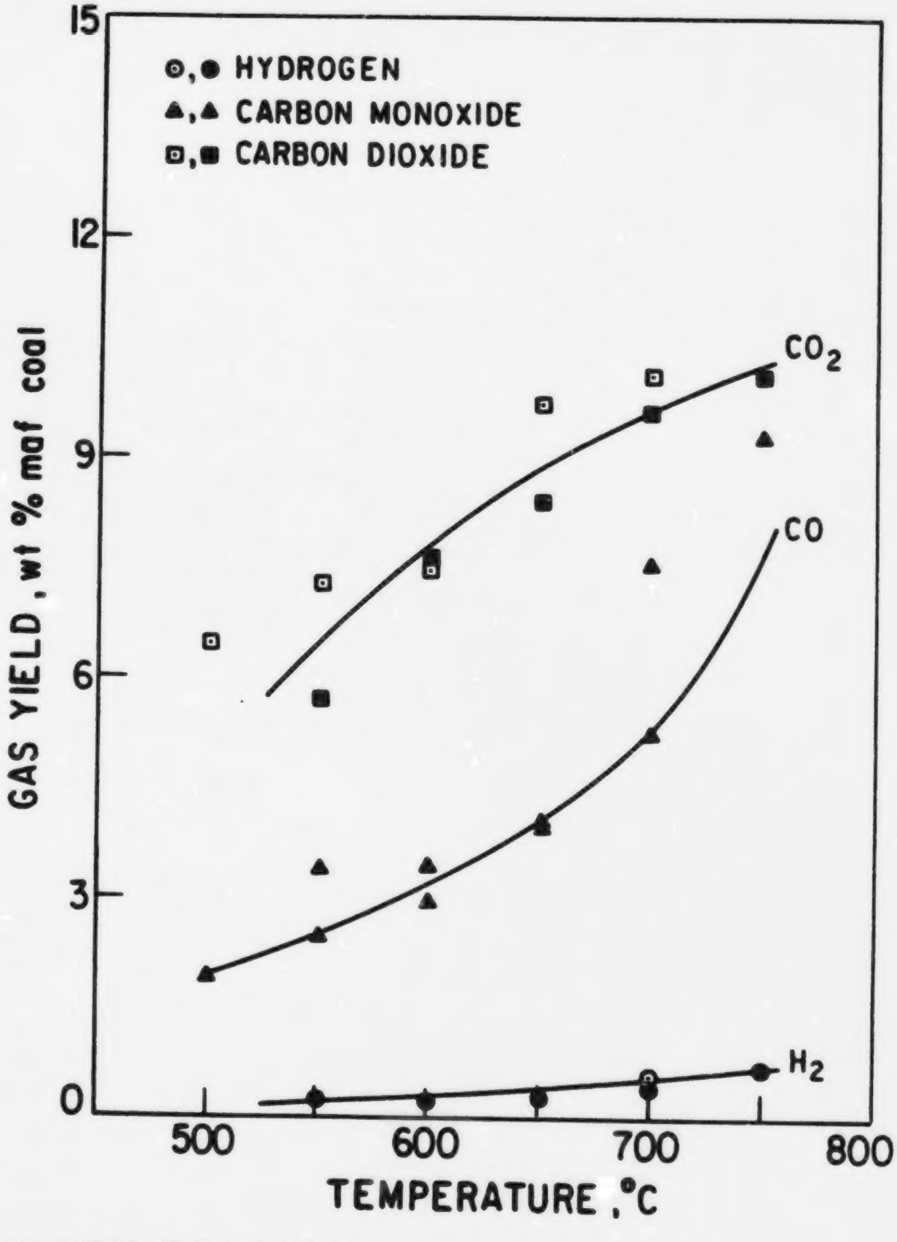

Fig. 15 – Gas Component Yields, Highvale Subbituminous, -149 +74 µm, N_2, 0.44 S. Open symbols, this work; closed symbols, previous work.

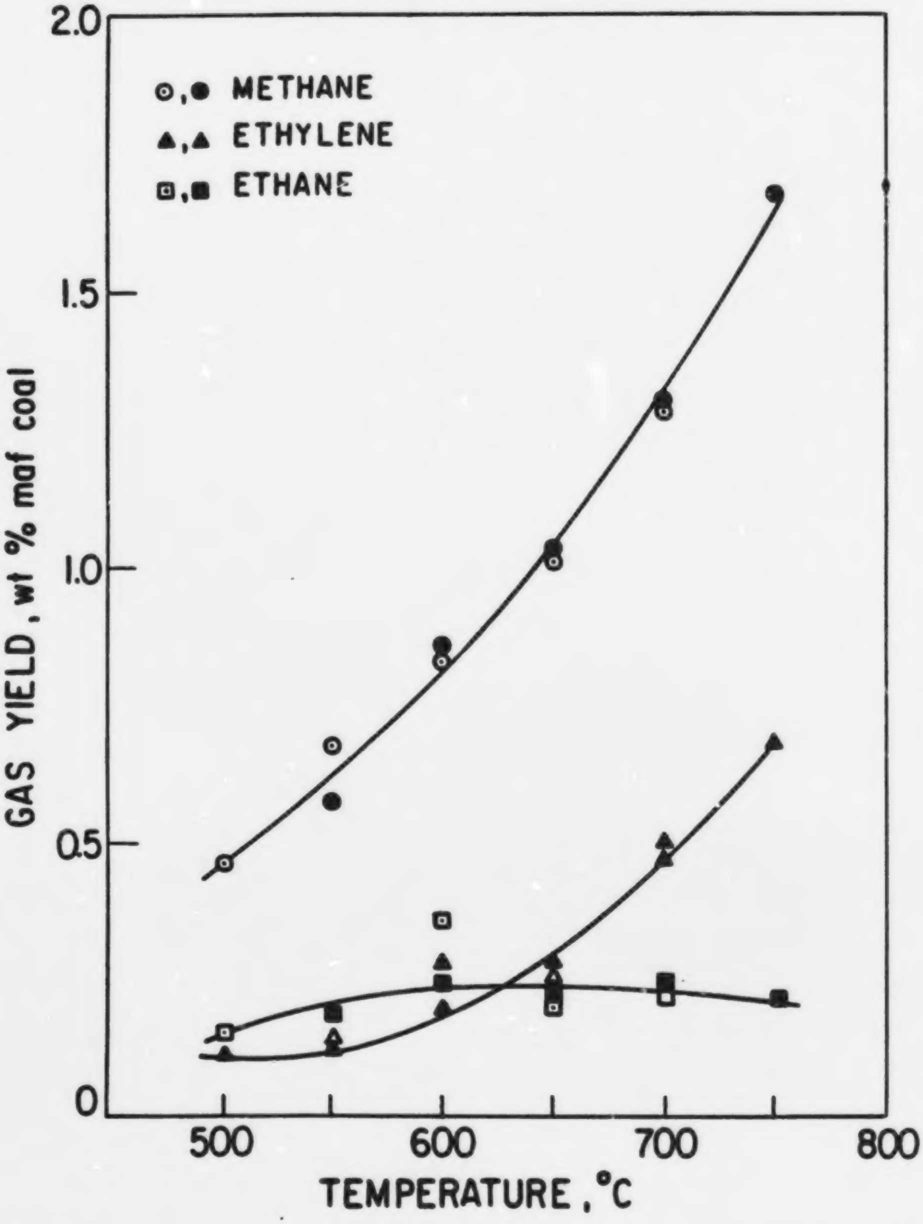

Fig. 16 – Hydrocarbon Gas Yields, Highvale Subbituminous, -149 +74 μm, N_2, 0.44 S. Open symbols, this work; closed symbols, previous work.

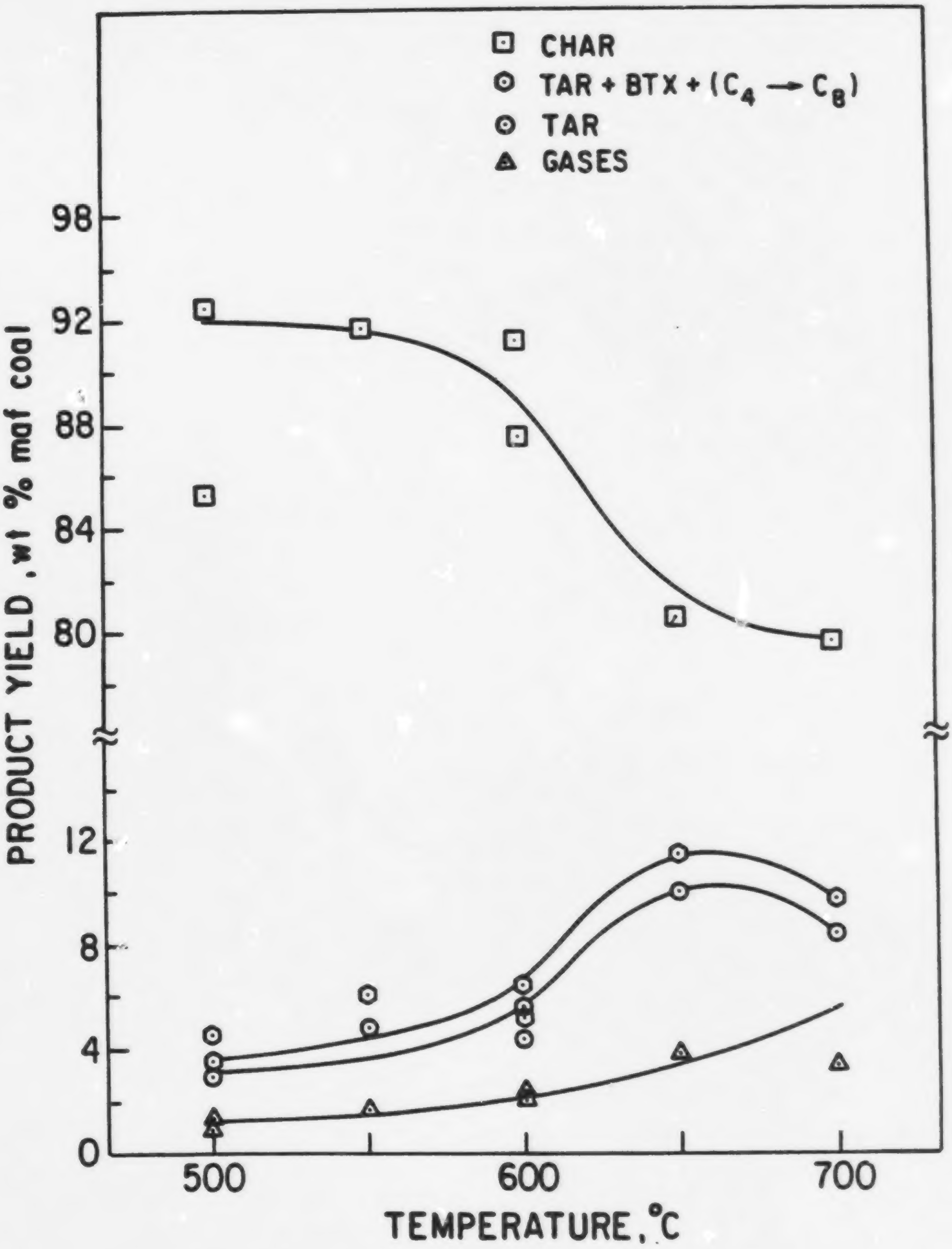

Fig. 17 – Char, Tar and Gas Yields, Balmer Bituminous, -149 + 74 μm, N_2, 0.8 S.

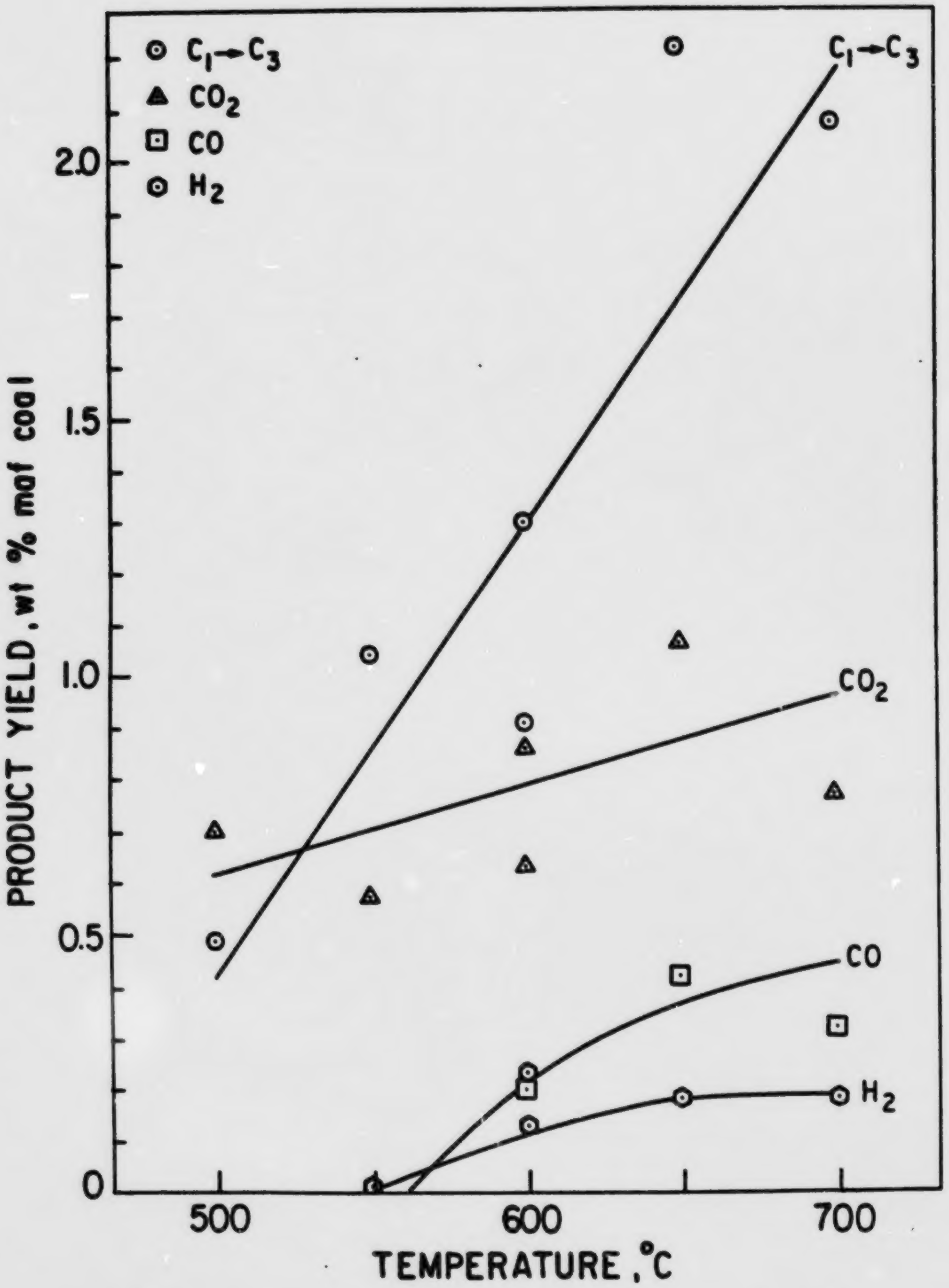

Fig. 18 – Gas Component Yields, Balmer Bituminous, -149 +74 μm, N_2, 0.8 S.

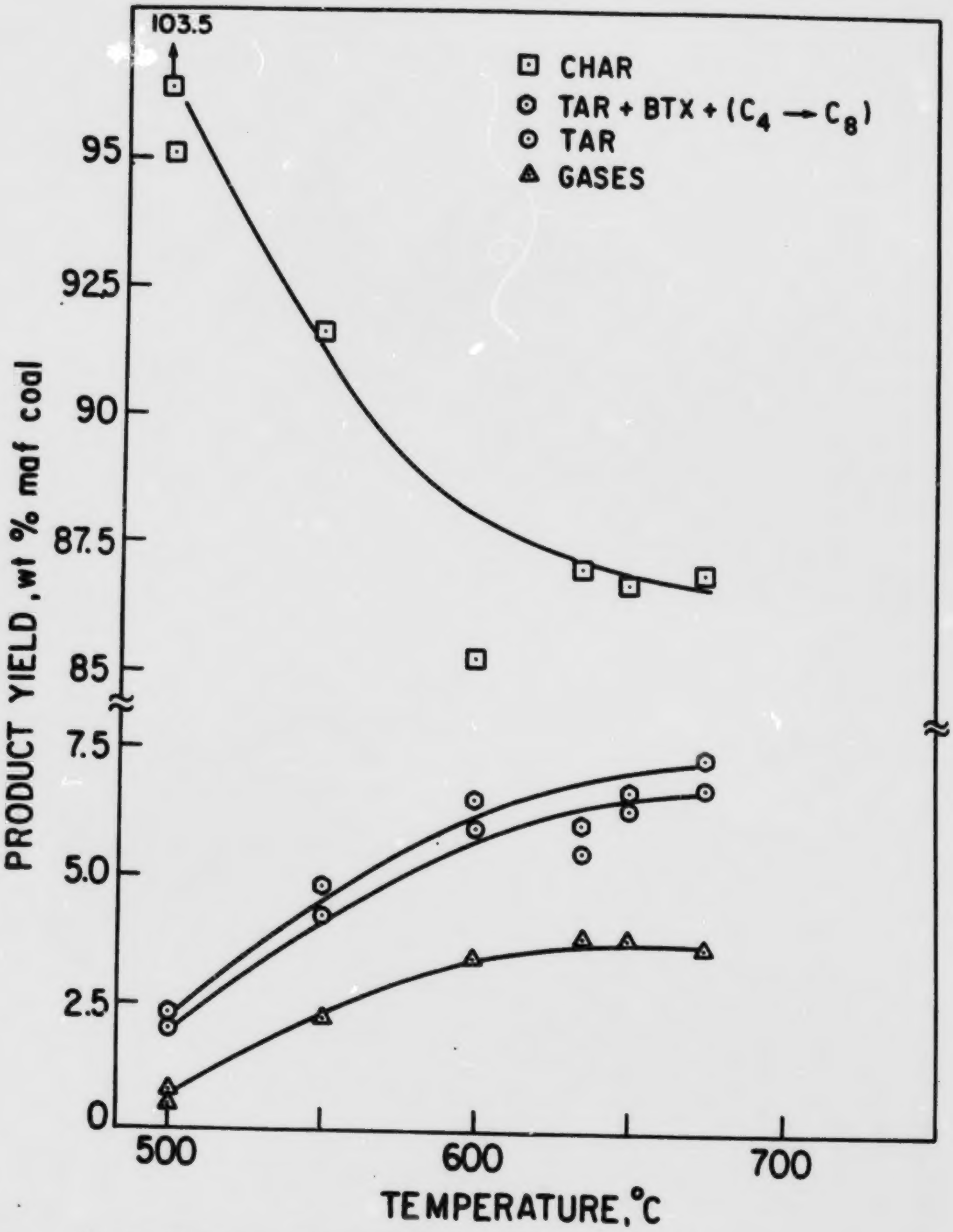

Fig. 19 – Char, Tar and Gas Yields, Macintyre Bituminous, -149 +74 μm, N_2, 0.8 S.

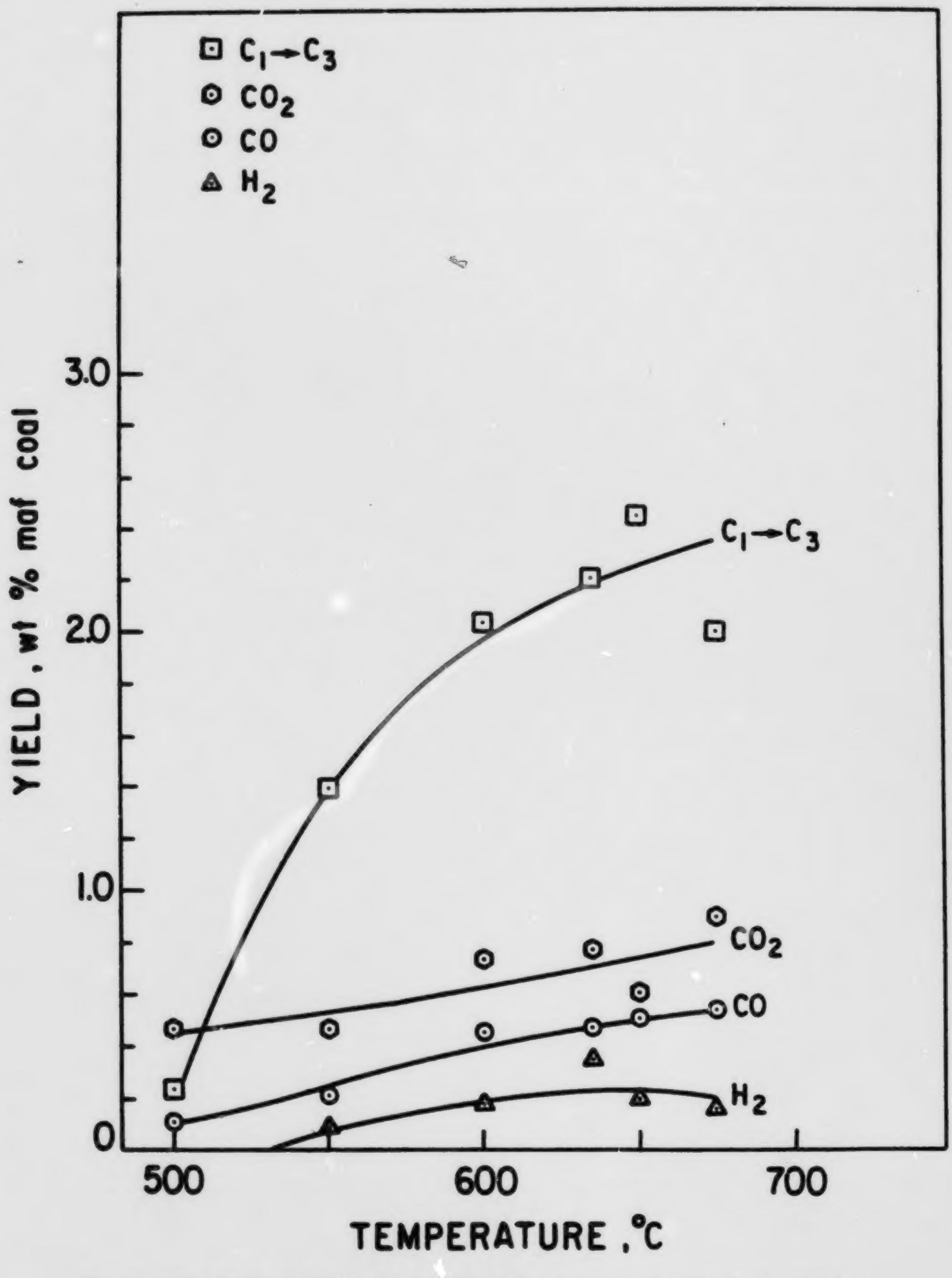

Fig. 20 – Gas Component Yields, McIntyre Bituminous, -149 +74 μm, N$_2$, 0.8 S.

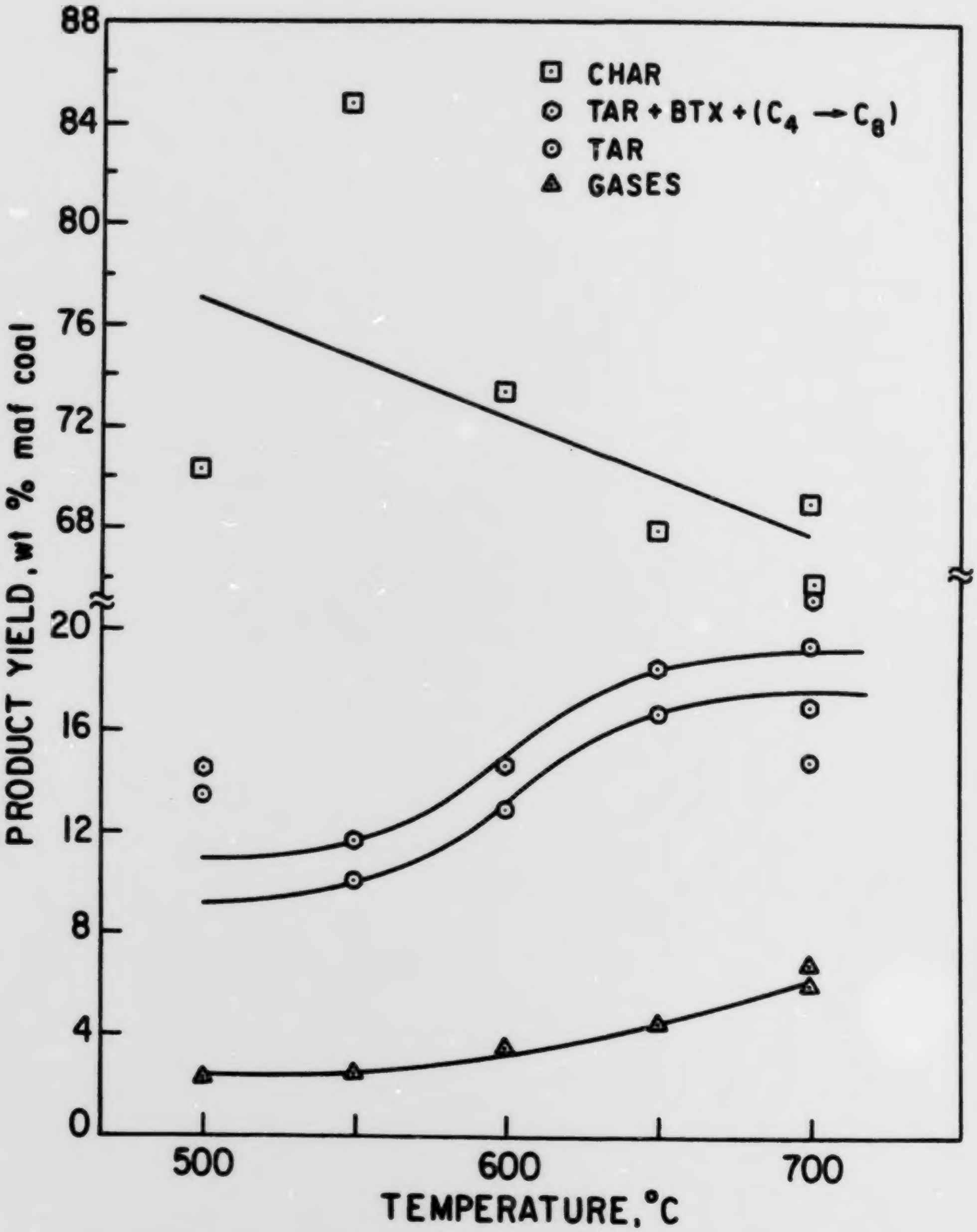

Fig. 21 – Char, Tar and Gas Yields, Devco Bituminous, -149 +74 μm, N_2, 0.8 S.

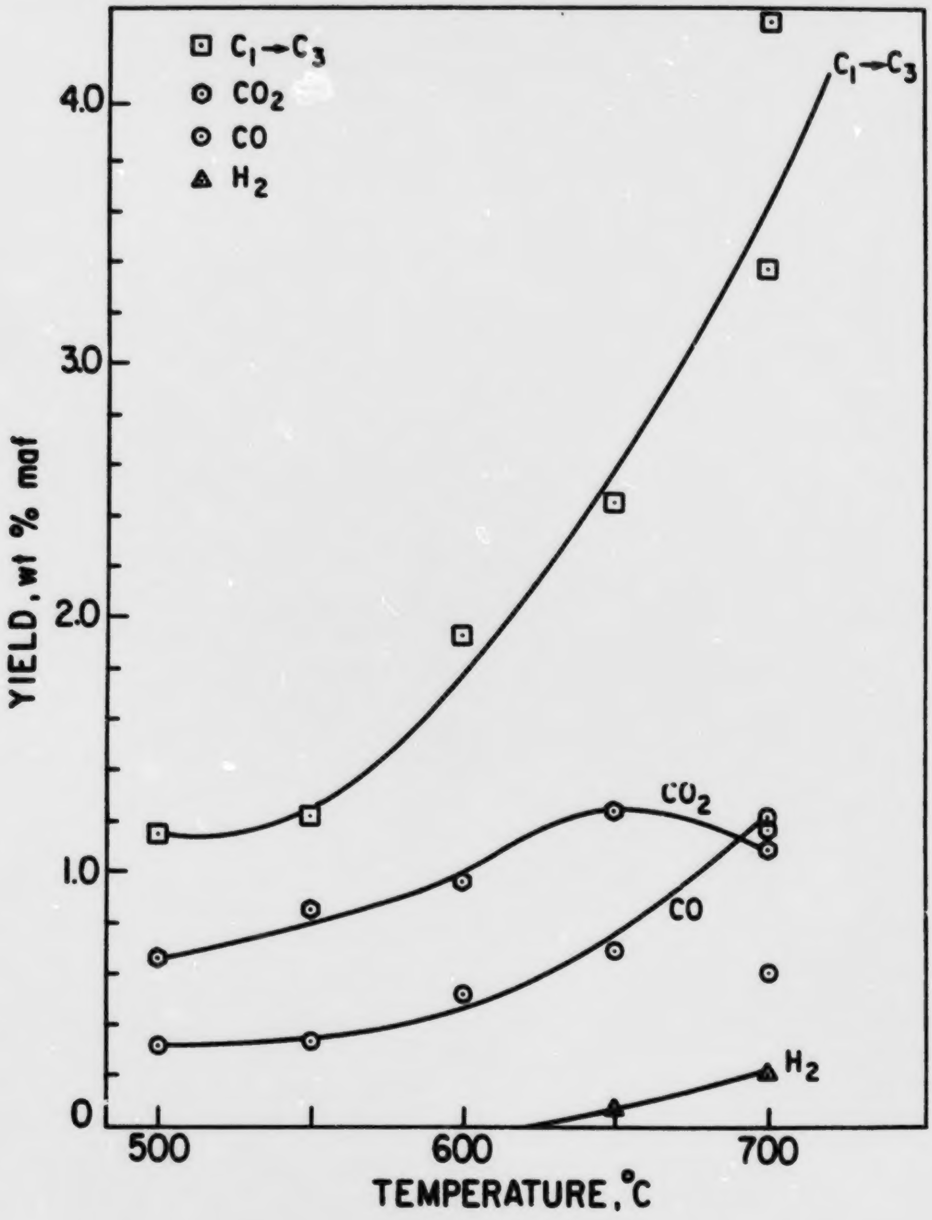

Fig. 22 – Gas Component Yields, Devco Bituminous, -149 + 74 μm, N_2, 0.8 S.

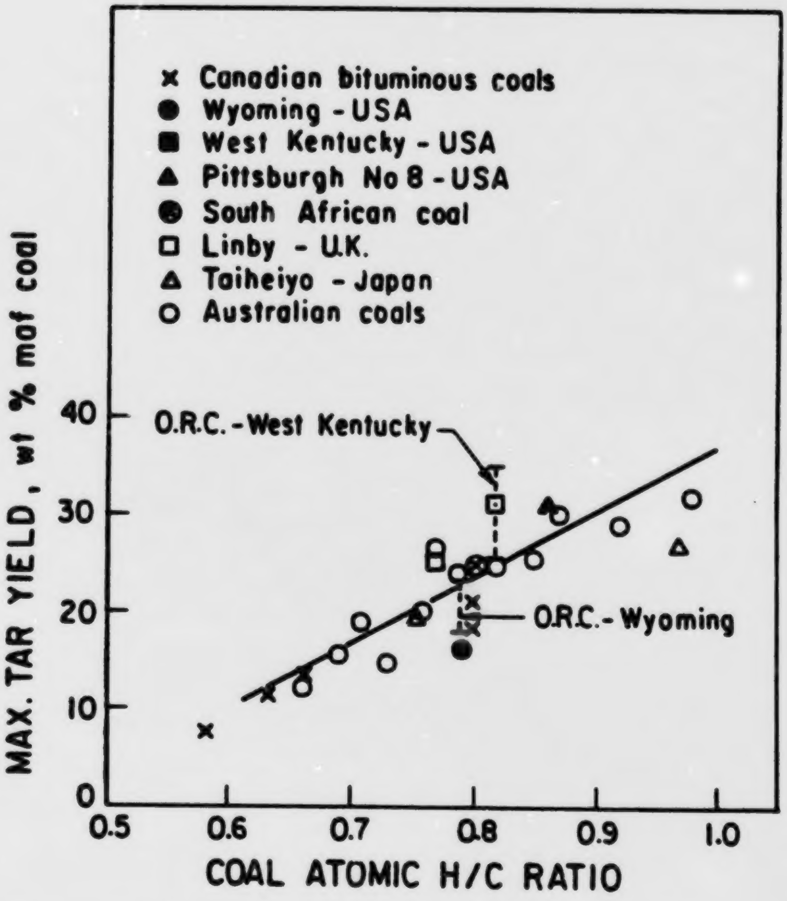

Fig. 23 – CSIRO Correlation of Maximum Tar Yields with Coal H/C Ratio for Bituminous Coals (from Smith, 1981), showing present results for Canadian Bituminous Coals.

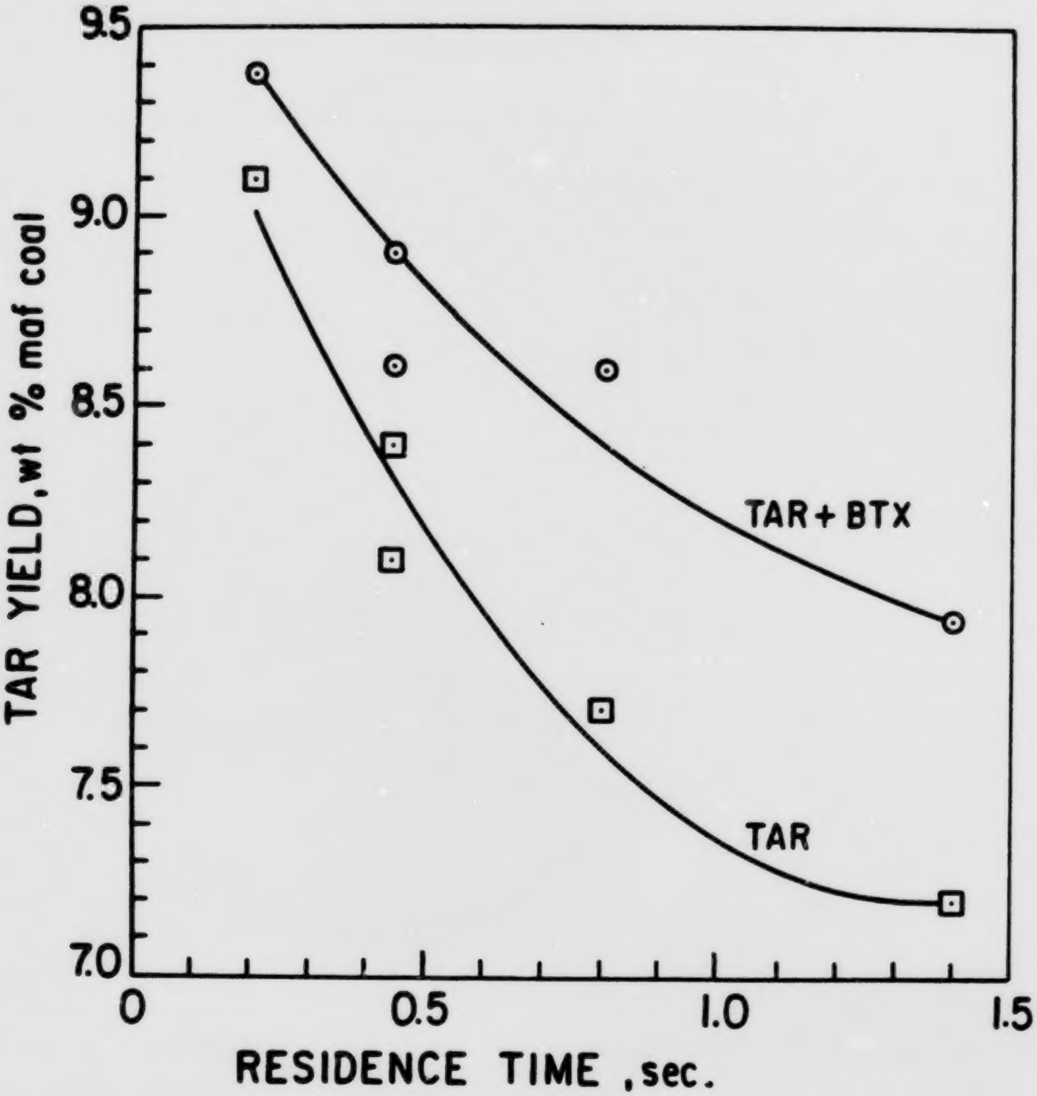

Fig. 24 – Effect of Residence Time on Tar Yields, Saskatchewan Lignite 3, -149 + 74 μm, N_2, 650°C.

SESSION III: PAPER 11

CHARACTERIZATION OF LIQUID FUELS FROM SPOUTED-BED PYROLYSIS OF CANADIAN COALS

K.C. Teo, D.J. Jung and A.P. Watkinson*
Department of Chemical Engineering
The University of British Columbia

ABSTRACT

Tar samples of predominantly hydrocarbon liquids were obtained from some representative Canadian coals of different ranks and regions. Hydrocarbon type and homolog type analysis was performed by a combination of solvent fractionation, flash chromatography, high-performance liquid chromatography with detailed characterization of fractions by high resolution (capillary) gas chromatography and mass spectrometry. The compositions of the hexane soluble fractions (oils) and benzene soluble fractions (asphaltenes) were characterized in depth. Some semiquantitative data on the hydrocarbon group type analysis were also obtained for the hexane extractable oils. In general, about 120 to 200 individual compounds, with the majority aromatic hydrocarbon in nature, were identified by a combination of HPLC elution sequence, HRGC retention index and mass spectra. The chromatographic profiles of major polynuclear aromatic hydrocarbon (PAH) series and the O, N and S-substituted heterocyclic PAHs present in the combined hexane and benzene soluble fractions were compared for a series of tar samples generated from the same coal under different pyrolysis temperatures.

**denotes speaker*

PRÉSENTATION 11

CARACTÉRISATION DES COMBUSTIBLES LIQUIDES OBTENUS PAR LA PYROLYSE SUR LIT À JET D'AIR DE CHARBONS CANADIENS

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Département de génie chimique
Université de la Colombie-Britannique

RÉSUMÉ

Des échantillons de goudron provenant de liquides surtout constitués d'hydrocarbures ont été extraits de certains charbons canadiens types, de régions et de rangs différents. L'analyse du type d'hydrocarbures et d'homologues a été faite en utilisant une combinaison de fractionnement au solvant, de chromatographie à l'éclair, de chromatographie liquide à grand rendement avec une caractérisation détaillée des fractions par la chromatographie au gaz à grande résolution (capillaire) et la spectrométrie de masse. Les compositions des fractions solubles d'hexane (pétroles) et des fractions solubles de benzène (asphaltène) ont été caractérisées de façon approfondie. Certaines données semi-quantitatives sur l'analyse du type de groupe d'hydrocarbures ont également été obtenues dans le cas des pétroles extractibles à l'hexane. En règle générale, on a identifié de 120 à 200 composés individuels, avec la majorité des hydrocarbures aromatiques en nature, grâce à une combinaison de séquence de décantation HPLC, à un indice de rétention HRGC et aux spectres de masse. Les profils chromatographiques des grandes séries d'hydrocarbures aromatiques polynucléaires (PAH) et les PHA hétérocycliques O, N et S-substitués présents dans les fractions solubles combinées d'hexane et de benzène ont été comparés, dans le cas de séries d'échantillons de goudron générés à partir du même charbon, à des températures de pyrolyse différentes.

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CHARACTERIZATION OF LIQUID FUELS FROM SPOUTED-BED PYROLYSIS OF CANADIAN COALS

INTRODUCTION

Thermal degradation processes for coal are significant not only for the practical utilization of coal via pyrolysis, but also as the initial step in combustion and gasification processes. Additionally, analytical pyrolysis gives information on the chemical structure of the coal. Among rapid-pyrolysis processes for liquids production, the spouted-bed pyrolyzer has been investigated at the bench-scale (1-5 kg coal/h) by A. Jarallah and Watkinson (1). In the present study (2) it has been demonstrated that the miniature-scale, continuous-feed spouted bed is a useful means of carrying out rapid pyrolysis of pulverized Canadian coals. Since comparable conditions can be used for different coals, with the exception of highly caking coals, these small-scale tests are of benefit for screening potential candidate coals for rapid pyrolysis processes, and for gathering information on pyrolysis products under a wide range of operating conditions.

Other than coal type, the major operating variable in a rapid pyrolysis atmospheric pressure experiment is the pyrolysis temperature. The particle size and feed rate show relatively minor effects over the operating range which is feasible on the miniature scale. The primary products of the pyrolysis - gases, tars (liquids) and char - must be characterized for each experiment. The tar liquids which have potential as refinery feedstocks present the major challenge in characterization. Because liquids from coal are extremely complex, to establish their structure they are usually fractionated into less complex mixtures or fractions prior to detailed characterization. To separate and identify an homologous series, or even individual compounds in these mixtures or fractions, is of some importance as these may determine the nature of the upgrading process to be applied.

In this paper, the effects of pyrolyzer operating variables are presented on the yields of total gas, of various gaseous species, of char and of total tar for the series of coals tested. The characterization of samples of the liquid product is then discussed. Tar liquids are mixtures of aliphatic, alicyclic, aromatic and heterocyclic aromatic compounds with a wide molecular weight distribution. The quality of the tar depends on the degree of coal metamorphism and on the pyrolysis processing conditions – in particular, the temperature and the residence time of tar vapour in the pyrolyzing zones.

Of the three types of pyrolysis product, analysis and characterization of the gases is most straightforward, almost routine. If the char from pyrolysis processes is to be burned to provide electricity, a minimal amount of char characterization in terms of proximate and ultimate analysis is justified. Methods are well established. Tars, on the other hand, are notoriously difficult and time consuming to characterize, and the development of methods and their application to the various feedstock coals provides the major focus of this study. The approach taken has been to assess the effect of coal type and pyrolyzer operating conditions on the quality of liquids produced by selecting certain typical samples rather than to attempt to characterize every tar sample produced.

EXPERIMENTAL PROCEDURE

Coal Pyrolysis

Four coals and a lignite were used as feedstocks for the present pyrolysis runs (Table 1). The experiments were carried out on the miniature spouted-bed pyrolysis unit shown in Figure 1 using coal of −250 + 125 μm size in most experiments. The reactor is 25 mm I.D. x 168 mm high. A charge of 20 g of −430 + 425 μm sand is put into the reactor and spouted by pre-heated nitrogen gas. Coal is conveyed via the micro-screw feeder into the apex of the reactor from the stirred feeder by the transport nitrogen. Volatiles and fine char exit through the top of the reactor, with the latter being separated in a glass cyclone. Coarse char may build up in the bed. The product gases were sampled downstream after the first impinger in a gas syringe every minute over a period of 5 or 10 minutes. Chromatographic analyses of the gaseous products were made using a Varian 6400 gas chromatograph equipped with Porapak N (60/80 mesh, 1/8" x 12') and Molecular Sieve 13X (60/80 mesh, 1/8" x 10') columns. The carrier gas was He or Ar at a flowrate of 20 ml/min under isothermal conditions (60°C or 80°C for Ar). For certain experiments, the H_2S contents of the gas were monitored by the lead acetate method. Gas yields were calculated from the gas analyses. Char was recovered from the cyclone and from the reactor and weighed to calculate the char yield.

Tar Liquids, Handling and Solvent Fractionation Procedure

The tar liquid collected in the series of impingers was first extracted with 75-100 ml HPLC grade n-hexane in an ultrasonic bath (~25°C/5 min). This hexane soluble fraction was clarified over a 0.45 μm micropore Teflon membrane filter and the filtrate was stored in a freezer (~−20°C) for further analysis. Fifty ml of HPLC grade tetrahydrofuran (THF) was used to remove the remaining tar materials under the same ultrasonic conditions. Typically, an estimated 1-3% of THF insoluble material (probably fine char particles) was observed. The THF soluble fraction after clarification was concentrated at ~65°C under reduced pressure (12-18 mm Hg) in a rotary flash evaporator to a volume of ca.1 ml. Thirty ml of spectroscopic grade benzene was added to the THF concentrate and extracted under the same ultrasonic conditions. The benzene solution was filtered over a pre-weighed 0.45 μm micropore Teflon membrane filter and the residue was washed (2 x 3 ml) with benzene. After drying, the weight of benzene insoluble-THF soluble was recorded. The combined benzene soluble fraction was subjected to similar evaporation conditions under reduced pressure at ~55°C. Great care was exercised to minimize any potential sample losses occurring in evaporating benzene solvent from the benzene soluble fractions. These losses could be substantial, due to the presence of material with boiling points below 150-120°C. Tar liquids obtained from shorter pyrolysis runs (<10-15 min) or from low feed rate (<1 g/hr) and from intermittent feed runs usually did not provide sufficient materials for solvent fractionation. The combined weight of extracts was defined as tar, and the yield calculated from the feed rate of the coal. Some water will be included in the THF soluble fraction. Closures on the gas, char and tar yields varied from 90% to 105%.

GAS, CHAR AND TAR YIELDS IN PYROLYSIS

Three variables of importance in coal pyrolysis runs other than coal type are pyrolysis temperature, particle size range and feed rate. For any given coal and pyrolysis unit, an optimal particle size range is probable. For all the tested coal samples in this miniature spouted-bed pyrolysis unit, the best size appeared to be −250 +125 μm. Coals, such as Fording, Minto and Devco which display a relatively high free-swelling index (FSI >6) tend to agglomerate with sand in the spouted bed and eventually prevent spouting, even at a high inlet gas velocity. For Fording coal, limited success has been gained only by conducting pyrolysis runs at very low feed rates (3 g/hr) with runs lasting ten minutes or less. Evidence was found of coal particles agglomerating with each other or adhering to the walls of the reactor, which suggested that the coal had undergone very rapid heating to above its transition mesophase on injection into the hot spouted sand bed. Gas analyses were generally repeatable, and since the tars were collected over the duration of the run for conditions where blockage had not occurred, it is believed that results are reliable where caking coals were used.

Gaseous Products

For subbituminous Forestburg coal, CO_2 and CO were produced in considerable quantities compared to the yields of methane, ethane, ethylene and acetylene. Undoubtedly, this is due to the high oxygen content (17.7 wt % dmmf) in the coal. Temperature effects on methane and ethylene gas yields were not changed significantly by the feed rate for the particle size range −250 +125 μm (Fig. 2). When smaller particles, −125 +75 μm were pyrolyzed, the methane yield almost doubled; however, ethylene production seemed not to be affected. Ethane yields were low compared to methane and ethylene, and were found to decrease with increasing temperature, suggesting possible thermal cracking of ethane at temperatures higher than ~500-600°C. Acetylene appeared in detectable quantities only at temperature >500°C and increased in quantity as the temperature rose.

For the bituminous Fording coal (Fig. 3a), methane was evolved in the largest proportion of the total gas produced. Because of the low oxygen content (4.3 wt %, dmmf basis) of this coal, CO_2 and CO yields were considerably lower. The ethane and ethylene profiles generally followed those for Forestburg coal pyrolysis runs. Acetylene gas appeared in detectable quantities at temperatures >550°C and increased as the temperature rose. For Onakawana lignite (Fig. 3b), the production of CO_2 and CO exceeded that of methane at temperatures >500°C. Ethane, ethylene, acetylene and hydrogen were evident also in small or trace quantities, and their composition profiles closely resembled those of Forestburg or Fording coals.

Pyrolysis results of the high-sulphur (7.0 wt % dmmf basis) bituminous Minto coal (Fig. 3c) showed similar composition profiles for methane production to Fording coal. CO and ethylene were produced in considerably higher quantities than CO_2, in particular at temperatures >700°C. Production of hydrogen, ethane and acetylene was found to increase with increasing temperature, particularly above 700°C. H_2S was produced in appreciable quantity.

In the case of low ash (2.1 wt % dried basis) bituminous Devco coal (Fig. 3d), the production of ethane exceeded that of methane, CO and CO_2 above 700°C. CO and CO_2 were found to be present in about equal amounts. The acetylene was produced in considerable quantities even at the low temperature of 450°C.

The ratios of C_2H_4/C_2H_6 and C_2H_2/C_2H_6 were calculated as a function of the pyrolysis temperature (2). As expected from the thermolysis of pure ethane, ratios of C_2H_4 and C_2H_2 relative to C_2H_6 usually increased substantially as pyrolysis temperature increased from 500-600°C. Higher feed rate and smaller particle size for Forestburg coal somehow favour the formation of C_2H_4 and C_2H_2. Fording coal and Onakawana lignite both produce more unsaturated species at higher temperatures. Minto coal shows some scatter in the ratio of C_2H_2/C_2H_6, which might be due in part to its high sulphur content (ca. 7.0 wt % dmmf basis). The high concentration of H_2S in the gaseous products seems to inhibit acetylene formation. It has been demonstrated that the H_2S has a profound effect on hydrocarbon pyrolysis and alters the rate of hydrocarbon cracking, hence affecting product distribution.

In summary, the formation of H_2, CH_4, CO and CO_2 in the gaseous products is always favored at temperatures higher than 550-600°C. Perhaps this tendency is at the expense of fixed carbon via the various gasification processes. Rapid spouted-bed pyrolysis also favored the formation of C_2- gases. In the presence of high H_2S and possibly other S-containing gaseous species concentrations, as reflected in the case of Minto, promotion of hydrogen, CH_4 and C_2-gases yields seems very likely.

Char and Tar Yields

Char quality is best assessed by comparison with the parent coal from which it was produced. Definitely its calorific value increases with fixed carbon content, while the volatile matter decreases with increasing severity of the pyrolysis. TGA analysis of chars derived from Forestburg, Fording, and Onakawana lignite, Devco and Minto coals have been reported (2). For a given particle size range, as feed rate goes up the volatiles remaining in the char increase, and the fixed carbon decreases.

Comparison of the volatile contents of chars from Onakawana lignite and Forestburg subbituminous coal suggests that at the same pyrolysis temperature, devolatilization proceeds to a lesser extent in the lignite. For example, devolatilizations of Forestburg coal at ~440 and 660°C are ~47 and ~60%, respectively, while Onakawana lignite proceeds only to about 35 and 40% under the same conditions. This is rather surprising if one relates reactivity to rank and/or H/C ratio. However, the degree of volatile depletion is not a true reflection of the tar-producing potential of a coal.

Table 2 shows the two highest tar yields from each of the tested coals. Tar liquid yield as high as ~40% can be achieved; the average is ~34% yield on coal fed basis. The net dry tar constitutes 20% to 80% of the collected tar liquids. The trend of the volatile contents associated with the chars and the general trend of gas yield increases with the rise of pyrolysis temperature, suggest that tar yield increases substantially with temperatures in the range ~500-700°C for the three bituminous coals (cf. Fording, Devco and Minto). For the subbituminous Forestburg coal, tar yields seem to be less dependent on the pyrolysis temperature over the range 500-600°C. Lignite seems very poor in net dry tar yield as water is the major component (>70%) in tar liquids. This is strongly related to the highly oxygenated aliphatic contents associated with the structure (3a).

CHARACTERIZATION OF HYDROCARBONS IN COAL TARS

Among the many publications in the current literature on coal pyrolysis, several (2-11) indicate the complexity of the hydrocarbon groups in the coal and its pyrolysis tar liquid products. The structures of coal tar liquids can differ substantially with the rank of the coal, and to a lesser extent with the pyrolyzing conditions. Coal tar liquids, despite severe bond-breaking in the pyrolysis process, are mixtures of widely different compounds. These compounds fall into four major categories: aliphatic hydrocarbons, aromatic hydrocarbons, polar aromatic compounds with functional groups, and heteroaromatic compounds and their derivatives.

Adaption of the American Petroleum Institute (API) RP-60 methods to the characterization of coal-derived liquids is possible, provided that a sample of 5g or more is available for the elementary boiling range separation into three boiling cuts (b.p. <200, 200-325, 325-475°C) and a residuum (475°C +). With the small tar samples (<2 g) obtained in this work, solvent fractionation is more appropriate, and though its nature is different from that of boiling point, yet it complements the boiling curve information. Solvent fractionation forms the elementary process of separating tar liquids into oils (n-hexane soluble fractions), asphaltenes (benzene-soluble fractions) and pre-asphaltenes (THF-soluble fractions) prior to detailed and sophisticated chromatographic sub-fractionation and characterization. In this paper, the emphasis is on the detailed characterization of aliphatic, alicyclic and aromatic hydrocarbons (1 to 5 ring system).

Small samples of hexane soluble fractions and hexane insoluble-benzene soluble fractions were prepared. These fractionated liquids were subjected to detailed compositional analysis by high-resolution capillary gas chromatograph (HRGC) in combination with high-performance liquid chromatography (HPLC) and HRGC-mass spectrometry (MS). Detailed characterization and hydrocarbon-type analyses were conducted with particular emphasis on compound identifications. The benzene insoluble-tetrahydrofuran soluble fractions have not been characterized.

PONA analysis using high-performance liquid chromatography (HPLC) provides a rapid, accurate method of characterization and is applicable to samples of various complexity and boiling ranges (13-16). These techniques, with suitable modifications, can be applied to hydrocarbons derived from coal liquids. PONA analysis by HPLC can also provide clean subfractions of hydrocarbon classes for further detailed characterization by other analytical techniques, such as HRGC and GC-MS (17-18). The main purpose of any high-resolution chromatographic system is to resolve mixtures of components or compounds into the constituted pure components. In general, the chromatographic system can provide retention (time) data (19) which can serve as complementary information to GC-MS for the positive identification of the resolved or separated components. The availability of computerized capillary HRGC and GC-MS systems has led to an enormous increase in the use of this technique in fossil fuel research (10,18). Although solvent extracts and boiling cuts from fossil fuel sources can be fractionated into compound classes by highly selective chromatographic methods, such as PONA-type HPLC separations, identification of individual components usually requires the use of high-resolution capillary GC coupled with fast-scanning quadrapole mass spectrometers. The breakdown products from pyrolysis of coals are thus studied by GC-MS and related to the structural features of coals. In this study GC-MS identified 100~200 aliphatics and simple and polynuclear aromatic components. Oxygen, nitrogen and sulphur-containing compounds in coal liquids are under investigation.

Forestburg Coal Tars

Table 3 gives the tar yield and solvent fractionation results for a series of pyrolysis runs at different temperatures. Although the total yield of water and tar is about constant over the temperature range 500-600°C, the water fraction of the tar increases with temperature, and thus the desirable tar fraction decreases. The hexane soluble fraction of tar is over 80% of the total water-free tar, and is relatively independent of temperature between 500 and 600°C. This fraction was characterized in depth.

The HRGC chromatograms for the hexane soluble fractions obtained from five pyrolysis runs at different temperatures are shown in Figure 4. These chromatograms show a marked resemblance to each other given the different pyrolysis conditions. The HPLC hydrocarbon group type PONA analysis shown in Figure 5 also reveals the same. These HPLC PONA analyses, however, cannot provide as detailed compositional data compared to HRGC and GC-MS analyses, yet in their unique way were able to offer an insight into the trend of the various hydrocarbon classes present in these solvent fractions. The separation of aliphatic plus alicyclic hydrocarbons from the aromatics represented by alkylbenzenes, alkylnaphthalenes and alkylphenanthrenes in particular can be achieved. These HPLC and HRGC chromatograms provided sufficient evidence to demonstrate that the hexane soluble *oil* fractions from Forestburg tar liquids derived under different pyrolysis conditions have very similar hydrocarbon classes but are varied in their distribution.

Figure 6 shows the assigned HPLC PONA chromatogram of the hexane fraction derived from pyrolysis run FO3 (feed rate 20.9 g/hr, particle size −250 +125 μm, ~500°C). The 14 collected HPLC sub-fractions were concentrated carefully and analysed by HRGC and/or GC-MS. The HRGC chromatograms are shown in Figure 7. Sub-fraction #1 indicates larger aliphatic molecules elute first, followed by lower molecular weight members. Sub-fraction #2 shows an interesting feature in the 1-alkene/n-alkane pairs. Fifty-eight aliphatic hydrocarbons were identified in sub-fraction #2 by means of GC-MS. Normal alkanes from C_8 to C_{29} were found and exhibit maxima, at C_{15} and C_{23} on the selective ion monitoring traces (Fig. 8). The relative intensity of 1-alkene/n-alkane pairs favored the presence of 1-alkenes for carbon number <13, whereas for carbon number >13, n-alkanes predominate. Sub-fraction #4 begins the domination by the alkene-alkane pairs. Some 22 alkylbenzenes, together with a few cycloalkane derivatives and C_{18}, C_{23} to C_{29} n-alkanes, were identified by means of GC-MS. Selective ion monitoring (Fig. 8) clearly demonstrated the presence of toluene, ethylbenzene, xylenes, 6 C_3-benzenes and 11 C_4-benzenes. In sub-fraction #7, 37 C_1 to C_4 alkylnaphthalenes were identified along with 7 C_1 and C_2 alkyl/dibenzofurans, seven alkylbiphenyls and three hydroaromatics. Sub-fractions #8 to 14 are made up of 2-3 ring aromatics, dominated by alkyl-substituted naphthalenes and phenanthrene with some biphenyl, fluorene and anthracene derivatives. Since no GC-MS data are available, the number of compounds appearing in the HRGC chromatograms of these sub-fractions #8 to 14 can only be estimated. The number is expected to be in the order of about 30 to 50 per sub-fraction. Since the collection time of each sub-fraction was two minutes, compounds close to the chromatographic cuts usually also appear in the following sub-fraction.

The most distinctive feature of all the high-resolution gas chromatograms for the 14 separated HPLC PONA sub-fractions (Fig. 6 and 7), together with the detailed study of three GC-MS traces, was the presence of a large number of well-resolved chromatographic peaks corresponding to about 400 different species (2). Calculations based on the peak area counts for the total chromatographic peaks, excluding the solvent peak, and estimated weight per cent distribution of the amounts of materials present in the 14 eluted sub-fractions, are summarized in Table 4. It is interesting to note that the aliphatic hydrocarbons in sub-fractions #1, 2 and 3 amounted to about 50% by weight (hexane soluble basis) and alkylbenzenes and some biphenyls accounted for 24% (sub-fraction #4, 5 and 6), followed by alkylnaphthalenes 15% (sub-fraction #7 and 8). The remaining sub-fractions are likely to be dominated by alkyl-substituted fluorenes, phenanthrenes, anthracenes and benzofurans.

From the solvent fractionation data the tar liquids contained considerable proportions of hexane soluble oils in the order of 70-85 wt % (dried tar basis), which in turn are dominated by the alkylbenzenes (~40-55%). Undoubtedly, pyrolysis of this Forestburg coal under the most favourable conditions could provide an important source of alkylbenzenes in the approximate range of 3-5 wt % (as-received basis).

Semi-quantitative analysis of HPLC fractions of the hexane soluble fraction at two temperatures show the following breakdown in classes.

Run #	FO2	FO3
Feed rate, g/hr (pyrolysis temp, °C)	7.1 g/hr (543°C)	20.1 g/hr (497°C)
Particle size	−125 +75 μm	−250 +125 μm
Aliphatics and cycloalkanes	10%	50%
Alkylbenzenes	55%	24%
Naphthalenes, biphenyls	23%	16%
Fluorenes, phenanthrenes, anthracene	5%	19%

Summary data from the detailed GC-MS characterization of the hexane insoluble-benzene soluble fraction from FO3 tar liquids are presented in reference (2). The GC-MS trace given in Figure 9 shows the benzene fraction to be dominated by polynuclear aromatics of ring number 3 and 4. High 1-alkenes and n-alkanes (C_{15}-C_{29}) are also found, as are appreciable amounts of oxygenated species. Some 130 compounds have been identified.

Fording Coal Tars

The small quantities of tar liquids generated from some limited pyrolysis runs created some problem in getting the solvent fractionation results. More than 200 compounds were identified in the whole hexane soluble fraction from pyrolysis run FC2. Approximately 85% of the species in this solvent fraction were identified by the GC-MS method (Fig. 10). The majority of the identified compounds are alkylbenzenes, some alkyl-substituted benzofurans, alkenes and alkanes (n-C_{11} to ~n-C_{25}), alkyl-substituted naphthalenes, fluorenes, phenanthrenes, anthracenes, fluoranthene, and some benz(a)anthracene, chrysenes, pyrenes, benzo(a)pyrenes and benzo(c)phenanthrenes. The molecular weight of the identified compounds spans from 100 to ~250. The average molecular weight of aliphatics in this tar is ~30 units higher than that of the aromatics. The l-alkene and n-alkane series exhibit a maximum at C_{14} and C_{15} (Fig. 11). The alkene and alkane distribution is similar to the reported hexane fractions of Forestburg tars (see Figure 8) except that in the latter case a second maximum at ~C_{25} was also found. Unlike the hexane fractions of Forestburg coal tars, such as FO2, FO3 and FO6 which are enriched in lighter aliphatic and aromatic hydrocarbons, the polynuclear aromatic hydrocarbons (3-5 rings) associated with the Fording hexane fraction seem considerably higher. The abundant presence of these polynuclear aromatics might well reflect the mature metamorphism associated with bituminous coals, since similar finds were also noted for the eastern Bituminous Minto coal. In addition, the presence of some alkyl-substituted benzofurans reflects a low degree of oxidation with this coal. The benzofurans in pyrolysis are formed via dehydration coupling of a phenolic group with another hydroxyl or phenolic group.

Devco Coal Tars

In order to identify the hexane soluble and benzene soluble fractions on a more routine basis by high-resolution capillary gas chromatography, it was decided to use an improved chemically bonded silica-capillary column DB-5 to substitute for the SE-30 capillary column used for the Forestburg coal tar samples. Detailed identification for the aromatic and some heterocyclic components was attempted with the aid of the chromatographic retention index system of Lee et al. (19). Calibration standards (naphthalene, phenanthrene, chrysene and picene) were used in conjunction with some key compounds such as anthracene, acenaphthylene, acenaphthene, biphenyl, fluorene, fluoranthene, pyrene, benz(a)anthracene and some of their derivatives. With the aid of a computerized data system, some efforts have been made to integrate the retention index method and calibration standards, together with the knowledge of some of the GC-MS studies. An attempt has been made to achieve automatic identification of aromatic and heterocyclic compounds present in the coal-derived pyrolysis liquids, in order to generate an *automatic compound type classification*.

In the pyrolysis temperature range of 550-670°C, the overall tar yield increases; however, the hexane soluble fraction goes through a maximum. Benzene solubles decrease monotonically. The tetrahydrofuran soluble fraction is markedly higher for the 670°C sample. Higher pyrolysis temperatures seem to favour thermal cracking into lighter products and condensation-polymerization into material less soluble in hexane and benzene. The capillary HRGC chromatographic study of the hexane and benzene fractions concluded that the changed pyrolysis temperature does not greatly influence the major chromatographic patterns and hence the classes of polynuclear aromatic hydrocarbons and heterocyclic components present.

Benzene and alkylbenzene distributions in hexane and benzene fractions for the three pyrolysis runs DV02, 03 and 04 were studied. Yields of simple benzene, toluene and xylene compounds were low. About 45-50% of the hexane soluble fraction, and about 36-47% of the benzene soluble fraction, have been accounted for (2). Alkyl-substituted naphthalenes, biphenyls, phenanthrenes and N-heterocycles represent the most significant species in the hexane fractions. In the benzene soluble fraction, benzene, phenanthrene, N-heterocycles and pyrene are most common. The overall results were combined according to the solvent fractionation distribution and are shown in Figure 12 on the effect of pyrolysis temperature. From the plots it seems that the devolatilization of alkylbenzenes reached a maximum of ~550° and slowly declined towards higher pyrolysis temperatures. Devolatilization for most of the char polynuclear aromatics and heterocycles is seen to decrease with the rise in temperature. These observations might be attributed to the thermal cracking of larger molecules at higher temperature into simple species, such as gaseous products and benzenes.

For the benzene soluble fraction more than 180 GC-MS peaks were observed, among which some 160 compounds were identified. Selective ion monitoring has been used to assign the alkene and alkane series, and normal alkanes and 1-alkenes from C_{14} to C_{30} were found. Isoprenoid paraffinic hydrocarbons, 2,6,10-trimethyltetradecane (C_{17}) have been identified. The majority of the identified compounds are alkyl-substituted benzenes, naphthalenes, biphenyls, fluorenes, fluoranthenes, anthracenes, phenanthrenes, pyrenes, and benz(a)anthracenes, together with some phenols and benzofurans. Selective ion-monitoring traces for several classes of alkyl-substituted polynuclear aromatic hydrocarbons as well as for indoles, carbazoles, and acridines have been conducted to verify the presence of these homologs.

This examination of Devco pyrolysis tars can be summarized as follows:

1. As in the case of Forestburg, temperature variations in pyrolysis tend to shift the molecular weight distribution, but do not greatly affect the major chromatographic patterns observed. Effects on solubility in various solvents can be marked.
2. Identification has been made of about 45% of both the hexane soluble fraction, and the benzene soluble fraction. Naphthalenes, biphenyls, phenanthrenes, pyrenes and a group of N-heterocycles are prominant. The effect of pyrolysis temperature on the amounts of these species has been illustrated.
3. Some 160 compounds have been identified.
4. In comparison with Forestburg tars, Devco tars are higher in THF soluble, markedly lower in hexane solubles, and markedly higher in benzene solubles. Thus three-, four- and five-ring compounds are more prominant than with Forestburg pyrolysis tars.

Minto Coal Tars

Combined hexane and benzene fractionated product distributions for Minto tar liquids are plotted against temperature in Figure 14. As the temperature increases from 500 to 700°C, both the hexane soluble and the THF soluble fractions decrease, while the benzene fraction increases. The marked difference between tars produced at 700°C and 600°C should be confirmed by additional experiments. Yields of alkylbenzenes, in particular toluene and xylenes, seem to be favored at higher temperature. About 49-62% of the hexane soluble fraction, and about 52-56% of the benzene soluble fraction have been accounted for (2). Figure 14 shows fluorenes, biphenyls, anthracenes, quinolines, N-heterocycles, and in particular the phenanthrenes represent the most significant classes in the combined hexane plus benzene soluble fractions. As for the case of Forestburg and Devco coal tars, the different pyrolysis temperature does not greatly influence the classes of polynuclear aromatic and heterocycles. However, at high temperatures there is an obvious parallel increase of N-heterocycles with PAHs.

Solvent fractionation distributions show that the benzene soluble fraction dominates the high-temperature tars. This trend reflects the increase with pyrolysis temperature of certain compound classes (Fig. 14), in particular the phenanthrenes, fluorenes, anthracenes and N-heterocycles. The benzene and alkylbenzenes seem to level off at ~700°C. The presence of high H_2S concentration in the pyrolysis gas atmosphere and the association of species high in sulphur with the parent coal might have a role in influencing the trend of product distributions. The advantage or disadvantage of high-sulphur contents on the product distribution from rapid pyrolysis process, and therefore the quality of the pyrolysis tar liquids, needs to be further evaluated.

Overall the results illustrate that for tars from Minto coal:

- In comparison with Forestburg tars, Minto tars are markedly lower in hexane solubles (20% vs 80%), and strongly enriched in the benzene plus THF fractions.
- Low molecular weight benzene and alkyl benzenes account for less than 6% of the hexane plus benzene fraction.

- Between 50 and 60% of both the hexane and benzene soluble fractions have been identified; major constituents are the three- and four-ringed aromatics, with significant contribution from N-, S- and O-heterocycles. Aliphatics have not been reported and further work is required to complete the characterization.

CONCLUSIONS

Rapid pyrolysis runs on the spouted bed have been conducted for five Canadian coals from different geological regions. The relative importance of the coal rank, feed rate, coal particle size and pyrolysis temperature on the quality of tar has been studied in depth in terms of the detailed compositional analysis of the tar in conjunction with the other characterization, such as char proximate analysis and gas analysis. Rapid spouted-bed pyrolysis for smaller coal particles followed by rapid quenching of the hot volatiles is essentially responsible for the higher tar yield during the process. As a result, preservation of larger molecular fragments is probable upon their departure from the coal matrix.

Lignite is unlikely to be suitable for tar production by the continuous spouted-bed rapid pyrolysis, because of the low tar yield and the tar quality. Highly caking bituminous coals were not easily handled on the miniature scale, although prior work had shown feasibility on the bench-scale. The subbituminous coal, such as Forestburg, and probably the bituminous Devco coal seem to be suitable candidate coals for this type of process, in terms of tar yield, tar quality and ease of handling of the coal. From the viewpoint of oxygen and sulphur species, respectively, these two coals need more study.

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TABLES

Table 1 – Proximate and ultimate analysis of coal

PROXIMATE ANALYSIS						ULTIMATE ANALYSIS					
		Dried Basis				Analysis, wt % (a)					
Coal Type (a)	Analysis Method (b)	Residual Moisture	Volatile matter	Fixed Carbon	Ash Ash	Ash	C	H	N	S	O(b)
Forestburg	ASTM	16.16	41.51	51.21	7.28	17.82	61.53	3.65	1.31	0.41	15.28
	TGA	12.09	40.67	52.03	7.30	–	76.19	4.52	1.62	0.50	17.67
Fording	ASTM	1.40	26.06	64.00	9.94	9.89	78.84	4.67	1.25	0.64	4.71
	TGA	1.32	22.08	65.88	12.04	–	88.27	5.23	1.40	0.71	4.33
Onakawana	ASTM	16.37	38.38	36.16	25.46	30.72	51.97	2.14	0.96	2.03	11.49
	TGA	17.41	42.35	32.38	25.37	–	77.77	3.20	1.44	2.93	17.59
	(c)	2.3	39.9	33.3	26.8						
Minto	ASTM	0.75	26.84	61.63	11.53	11.48	73.41	4.73	N.A.	6.22	4.16(c)
	TGA	1.11	35.00	53.65	11.35	–	83.80	5.40	N.A.	7.03	10.8 (c)
Devco	ASTM	1.10	29.16	68.73	2.11	2.17	83.73	5.38	1.80	1.46	5.46
	TGA	0.95	38.32	59.53	2.15	–	85.74	5.51	1.84	1.49	5.42
	(c)	1.90	37.5	59.7	2.8						

(a) *All coal samples were grinded to pass Tyler #60 mesh screen (i.e. – 250 μm)*

(b) *ASTM method was performed by Mr. Peter Kampe of Mining Engineering(U.B.C.) on a Fischer Coal Analyser (model 490); TGA method was performed in-house on a Perkin-Elmer Thermal Analyser (TG-2)*

(c) *Recalculated from reference (by E. Furimsky et al.)*

(a) *C, H, N on dmmf (Parr) basis; S on daf basis*

(b) *O (by difference) = 100 – (C + H + N + S) on dry basis*

O (by difference) = 100 – (C + H + N) for dmmf basis

(c) *Including N*

Table 2 – Maximum tar yield from spouted-bed pyrolysis of some Canadian coals

Coal Type	VM in parent coal, wt % (a) (ASTM)	Run #	Pyrolysis Temp, °C	Feed Rate g/hr	Max. Tar Liquid Yield wt % (a)	Comment
Forestburg	41.5	FO3	497	20.9	26.8	Moisture 38%
		FO6	600	14.1	23.6	Moisture 50%
Fording	26.1	FC3C	603	3.0	40.8(b)	–
		FC3B	551	3.0	31.0(b)	
Onakawana	38.4	ONO4	498	6.8	29.4	Moisture 70-80%
		ONO5	548	6.0	26.7	
Devco	29.2	DVO2	672	0.8	38.7	–
		DVO1	596	6.2	24.2	
Minto	26.8	MNO3	690	1.1	20.1	Heavy tar
		MNO2	498(c)	4.1	15.1	Heavy tar

(a) *As-received basis; tar liquid referring to raw tar contains water*

(b) *Estimated values*

(c) *Temperature indicated might be lower than actual temperature, due to agglomeration problem*

Table 3 – Solvent fractionated product distribution from Forestburg coal tars

Run #	FO2	FO3	FO4	FO5	FO6
Conditions					
Pyrolysis Temp, °C	448-647(b)	497	502	549	599
Feed Rate, g/hr (a)	11.8	20.94	13.20	13.02	14.07
Normalized Tar Liquid Yield wt %(c)	25.2	26.8	22.3	23.3	23.6
Water Content, wt %(d)	47.4	37.5	44.3	46.9	50.4
	Solvent Fraction, wt % dried tar basis				
Hexane Soluble	79.0	70.2	83.4	83.4	84.9
Benzene Soluble	21.0	23.5	13.1	13.2	12.4
Tetrahydrofuran Soluble		6.3	3.5	3.4	2.7

(a) Coal particle size range = −250 +125 μm for all runs, except FO2 (−125 +75 μm)
(b) Mixed temperature run at 448, 503, 532, 596, and 647°C (5 minutes/temperature point)
(c) As-received basis; tar liquid = organic tar + water
(d) Whole tar basis

Table 4 – Estimation of weight per cent distribution of HPLC-PONA sub-fractions from micro-preparative separation of FO3 hexane soluble fraction

Sub-fraction	Collection time min (a)	Estimated wt % distribution (normalized)	Major hydrocarbon class	Approximate alkyl substitution or (carbon #)
1	6.6-8.5	14.5	alkane	$(\sim C_8 - C_{29})$
2	8.6-10.5	28.1	alkene + alkane	$(\sim C_8 - C_{29})$
3	10.6-12.5	6.7	cycloalkane (?)	$(\sim C_{14} - C_{30}?)$
4	12.6-14.5	7.1	benzene	$(C_1 - C_5)$
5	14.6-16.5	10.8	benzene(b)	
6	16.6-18.5	6.4	benzene(b)	
7	18.6-20.5	11.3	naphthalene(b)	$(C_1 - C_4/C_5)$
8	20.6-22.5	3.9	naphthalene(b)	
9	22.6-24.5	0.8	naphthalene	
10 + 11	24.6-28.5	5.9	Fluorene +	$(C_1 - C_4/C_5)$
12	28.6-30.5	1.9	phenanthrene	
13	30.6-32.5	1.2	anthracene +	
14	32.6-34.5	1.4	benzofuran, etc.	

(a) Micropak PONA column (7.2 mm × length 30 cm); hexane flow rate = 1.2 ml/min
(b) Might contain some biphenyls

FIGURES

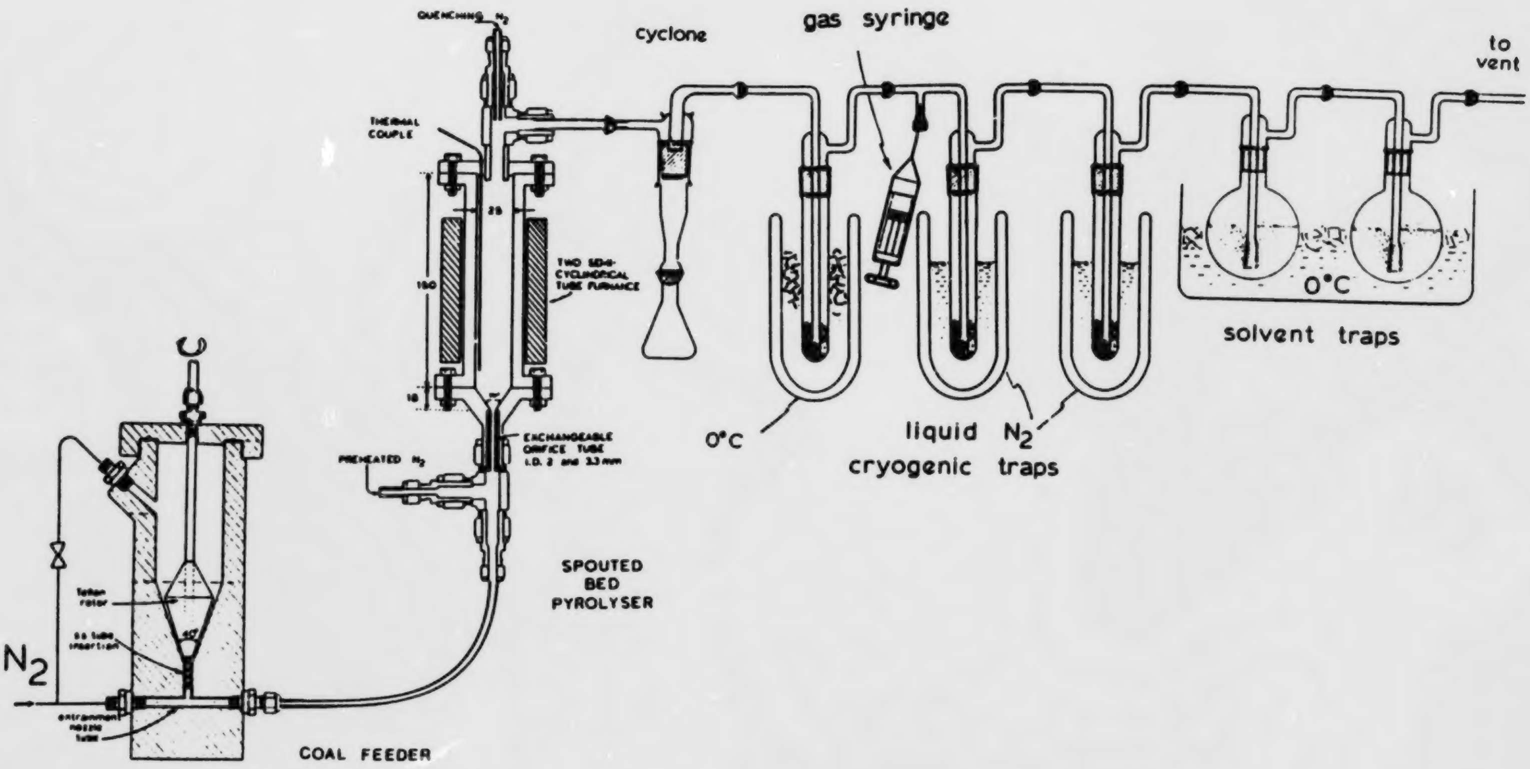

QUENCHING N_2
THERMAL COUPLE
28
150
10
TWO SEMI-CYLINDRICAL TUBE FURNACE
EXCHANGEABLE ORIFICE TUBE I.D. 2 and 3.3 mm
PREHEATED N_2
SPOUTED BED PYROLYSER
cyclone
gas syringe
to vent
0°C
liquid N_2
cryogenic traps
0°C
solvent traps
N_2
teflon rotor
ss tube insertion
entrainment nozzle tube
COAL FEEDER

Fig. 1 – Spouted-bed pyrolysis unit

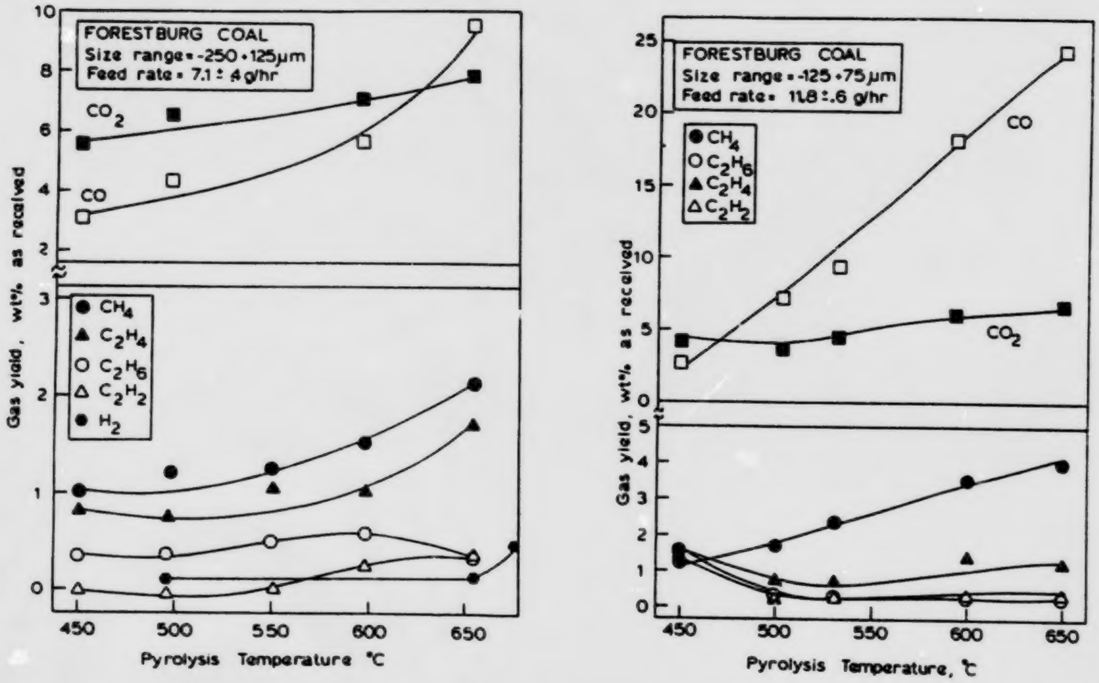


Fig. 2 – Effect of temperature on gas yield

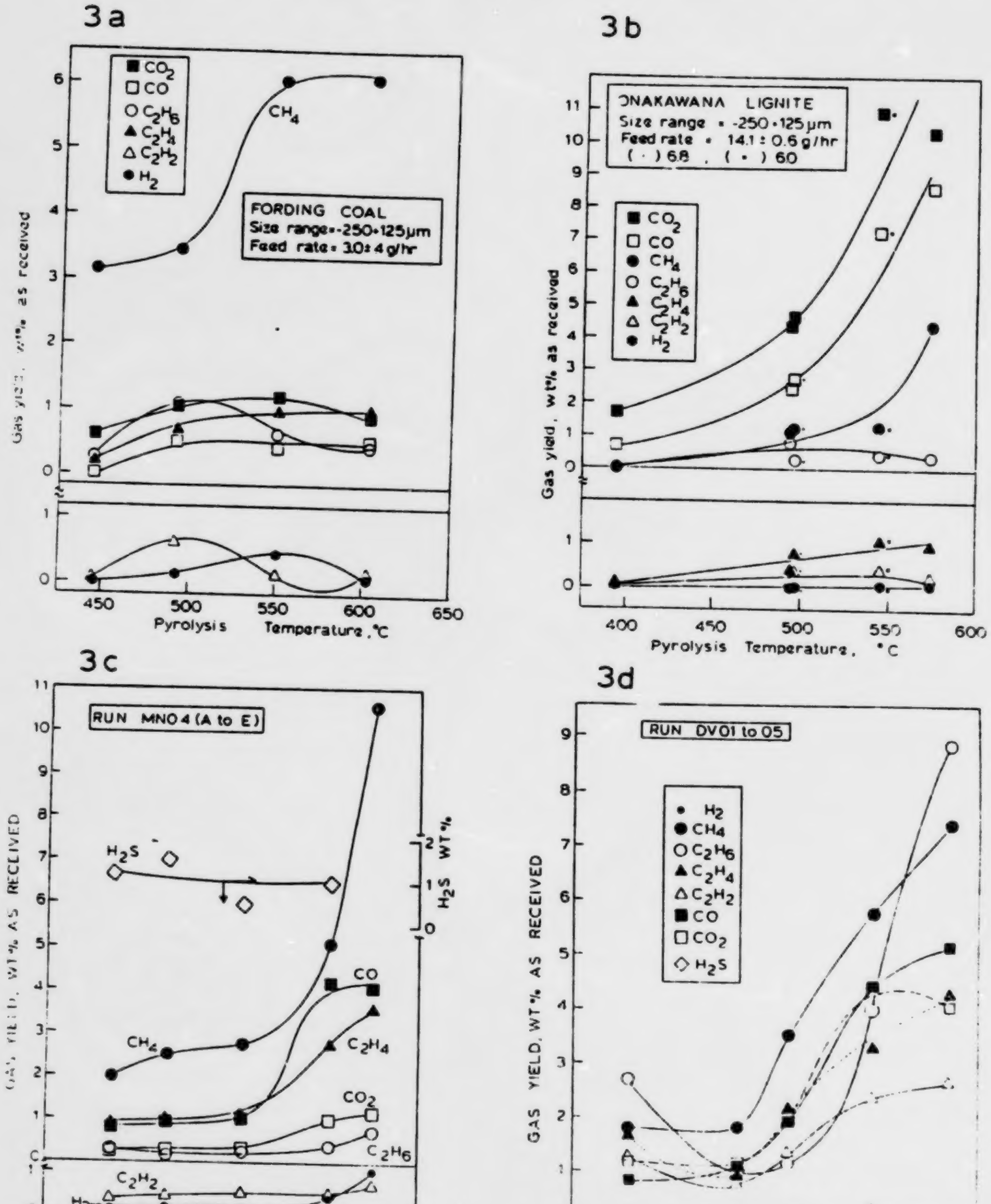
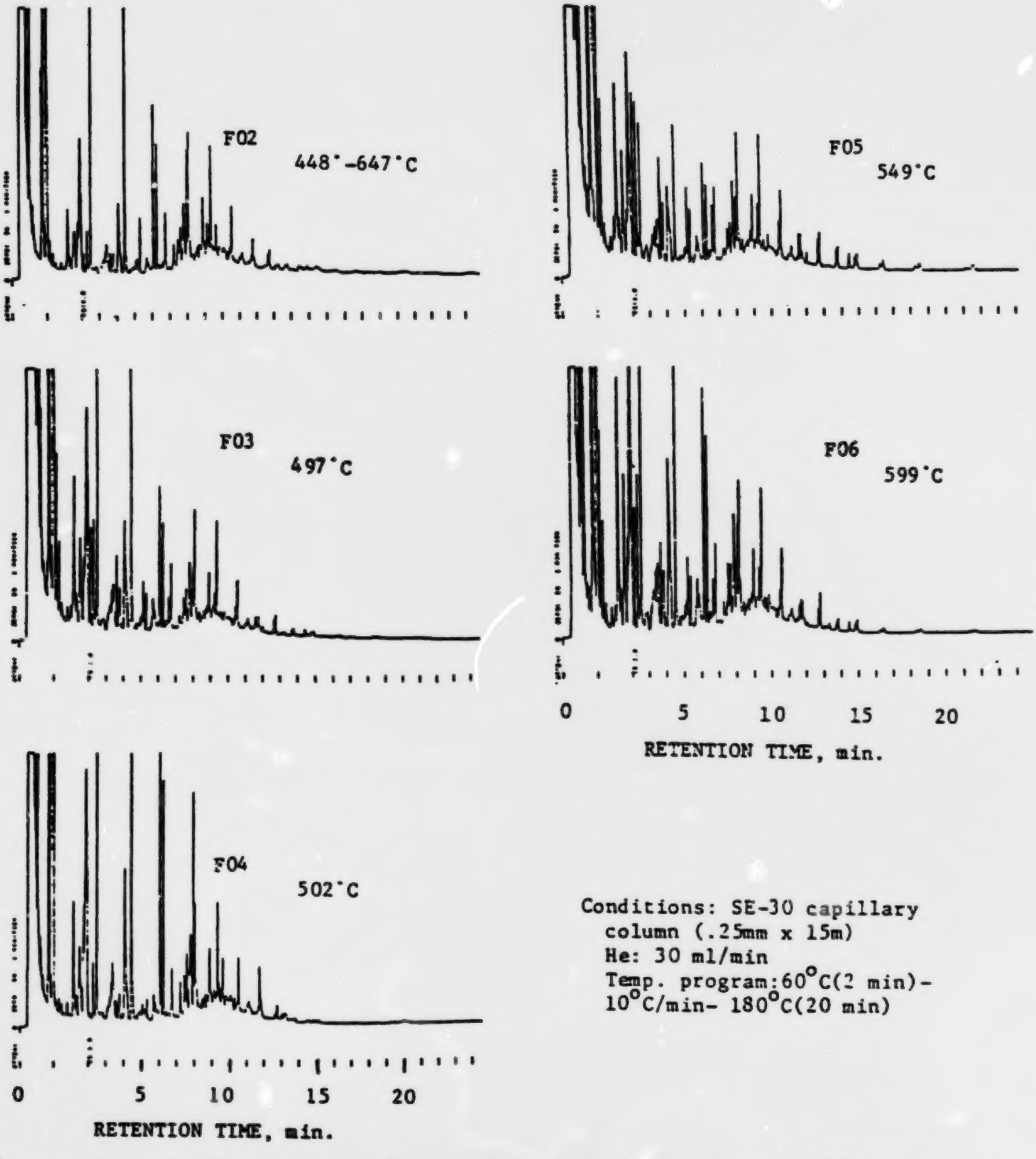


Fig. 3 – Effect of temperature on gas yield



Conditions: SE-30 capillary
column (.25mm x 15m)
He: 30 ml/min
Temp. program: 60°C(2 min)-
10°C/min- 180°C(20 min)

Fig. 4 – HRGC chromatograms of hexane soluble fractions from pyrolysis runs # FO2 to FO6

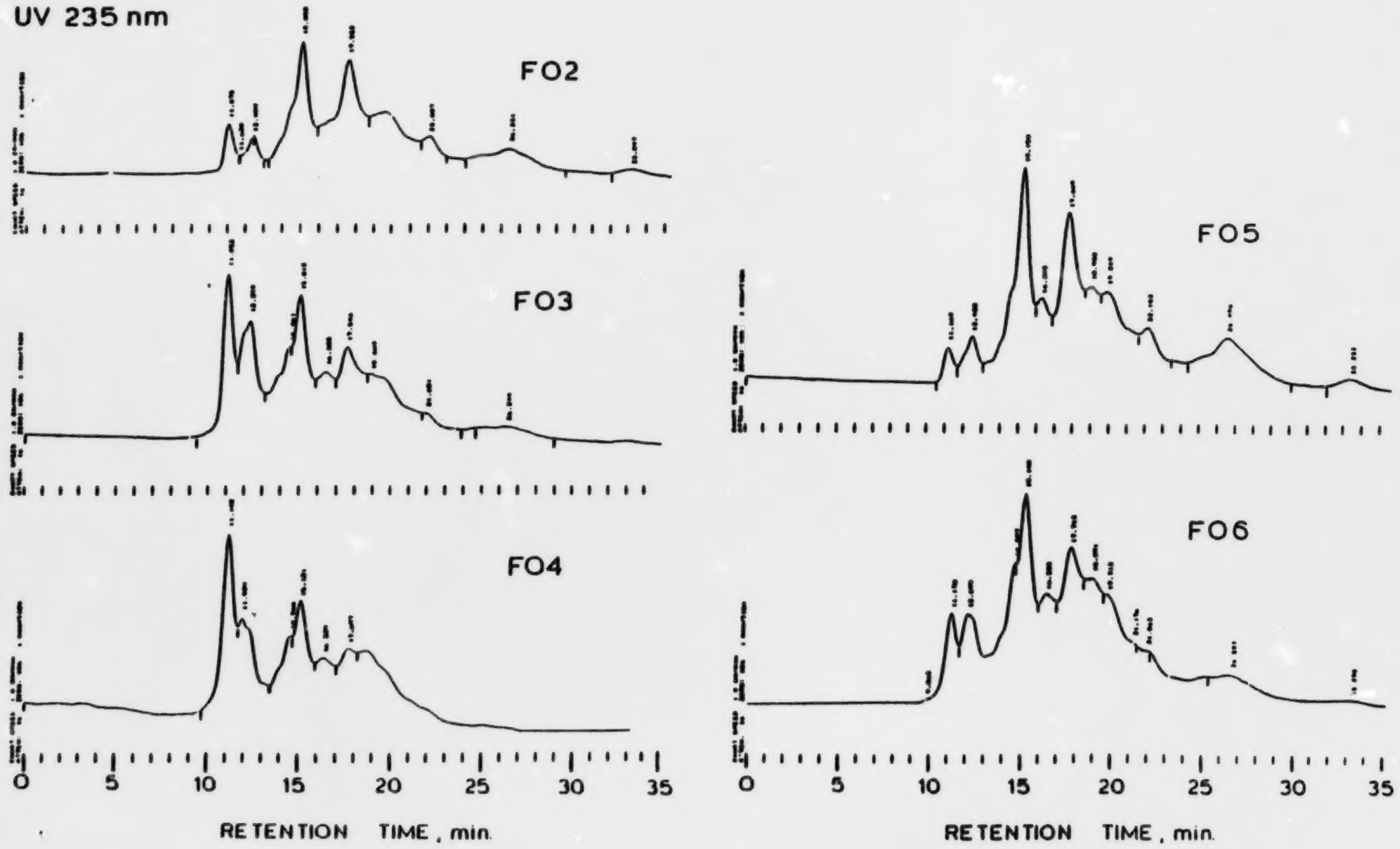


Fig. 5 – HPLC PONA analysis of the Forestburg coal tars - hexane soluble fractions

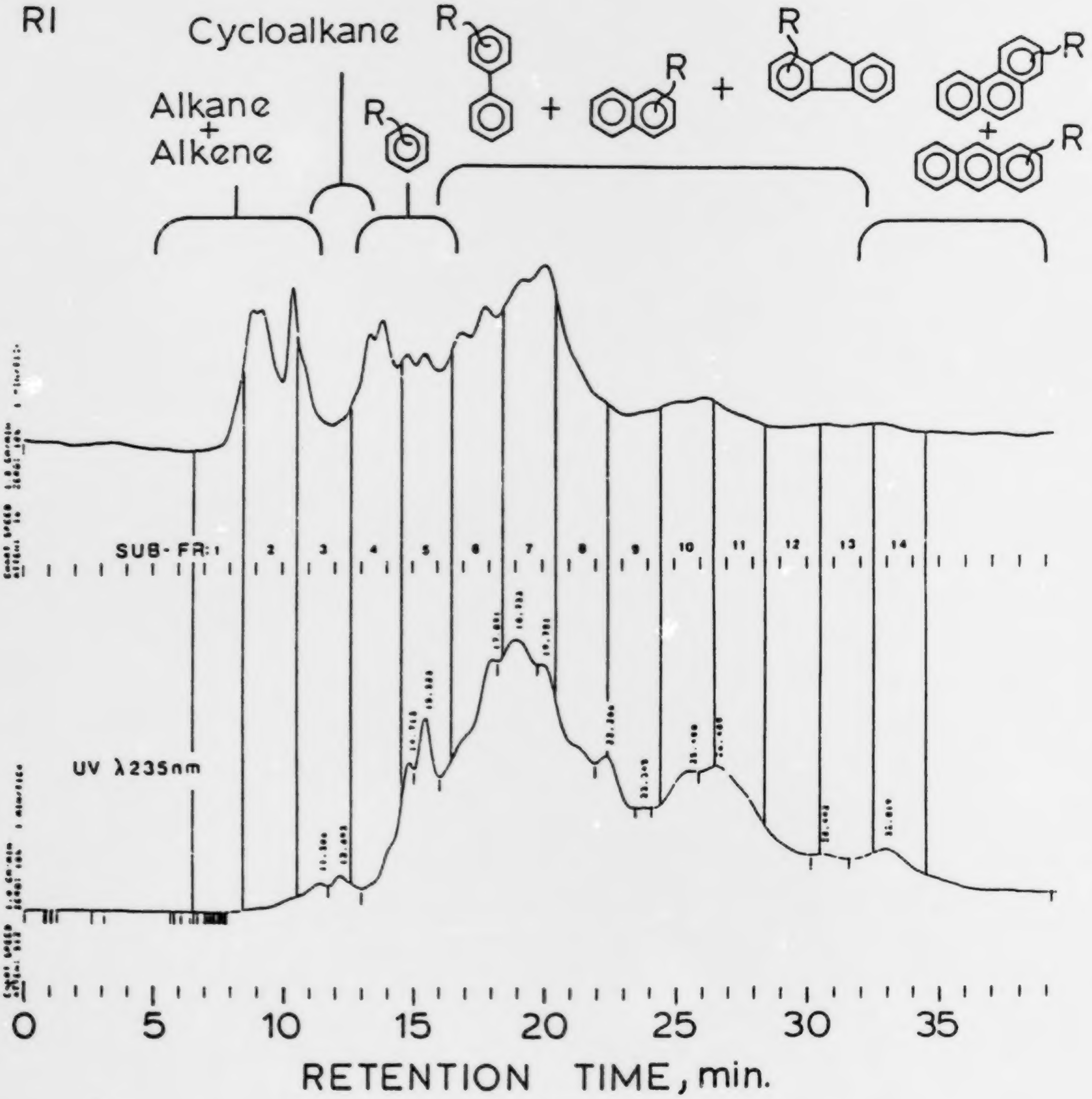


Fig. 6 – UV outputs for PONA separation of hexane soluble fraction from FO3

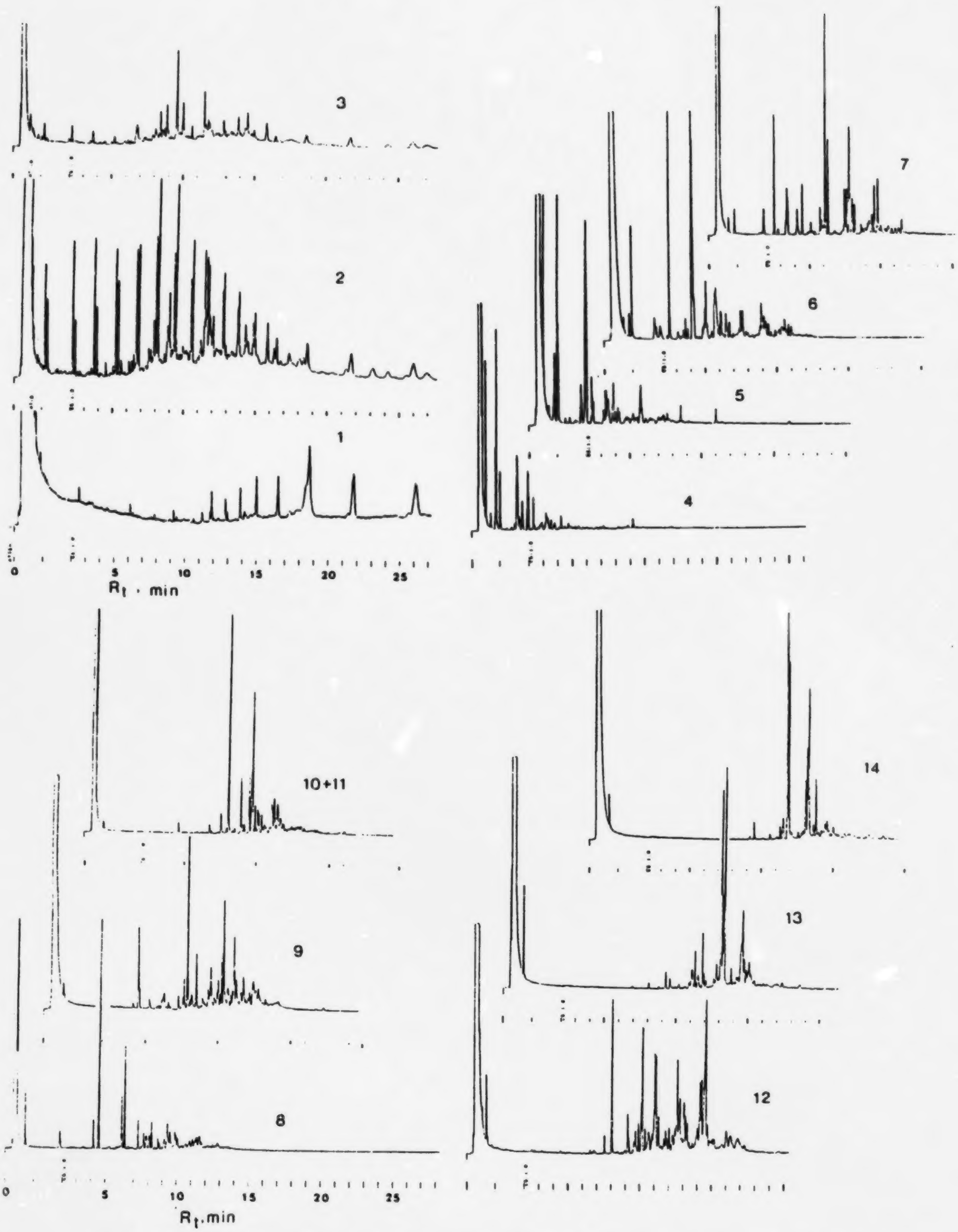


Fig. 7 - HRGC of PONA sub-fractions from hexane soluble fraction of Forestburg coal tar (run FO3)

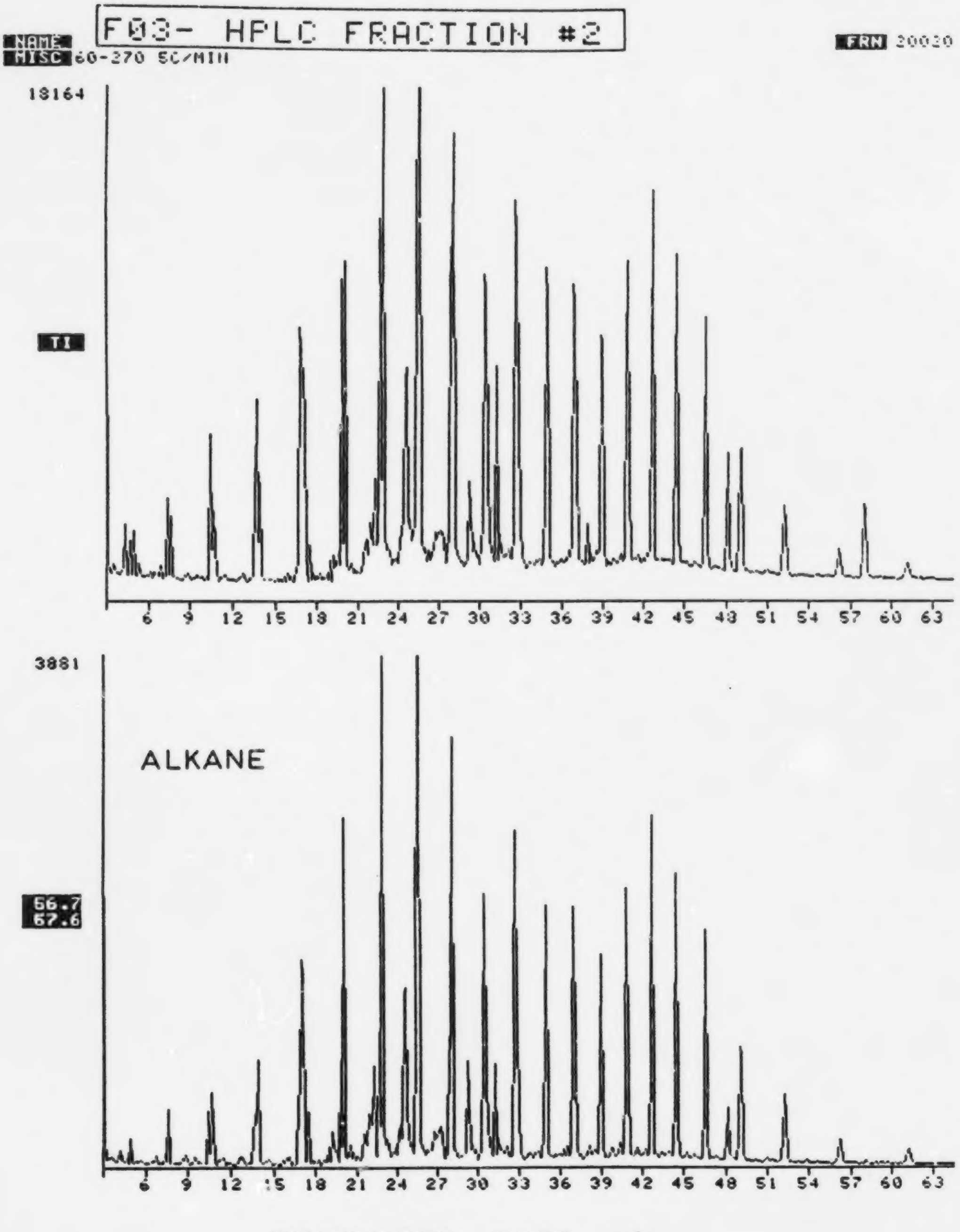


Fig. 8 – Total ion and selective ion-monitoring outputs on GC-MS analysis for HPLC sub-fraction 2 (FO3)

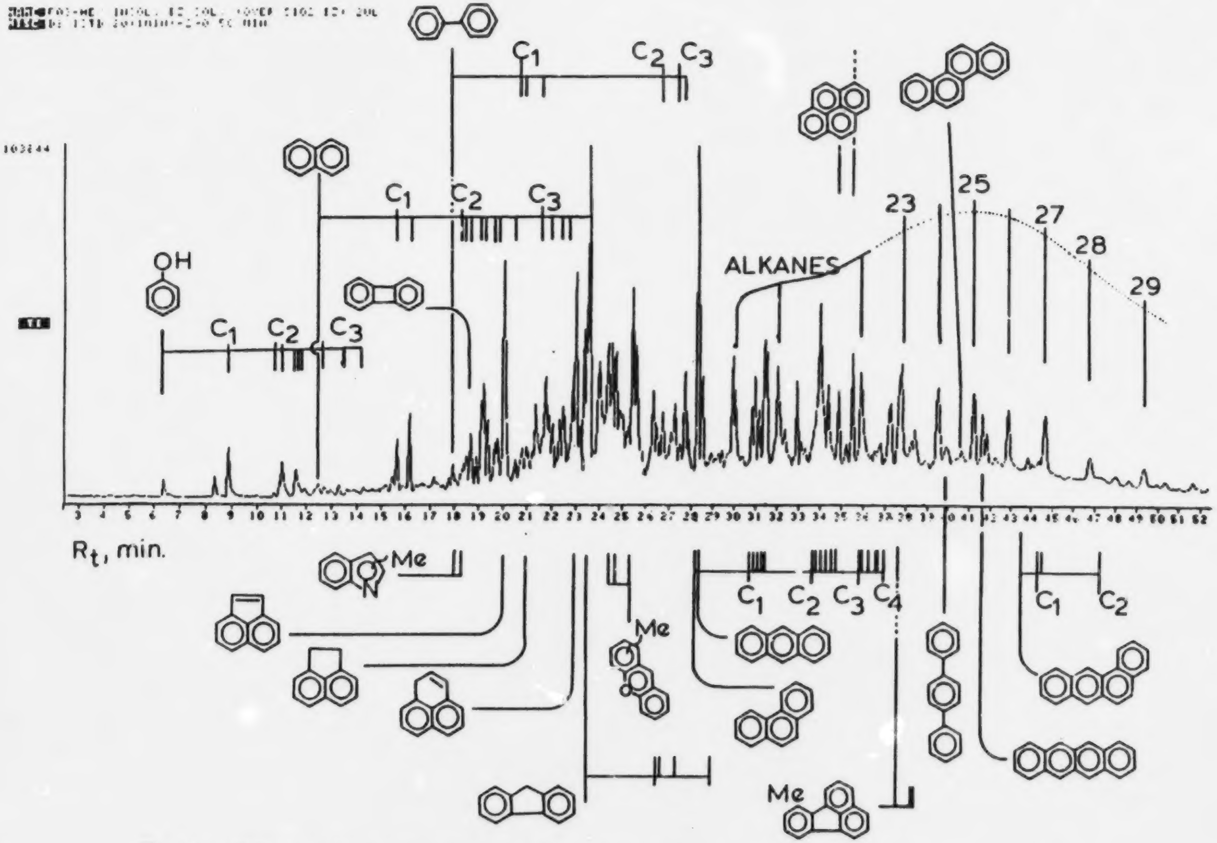


Fig. 9 – Total ion output on GC-MS analysis of Forestburg benzene soluble fraction (run FO3)

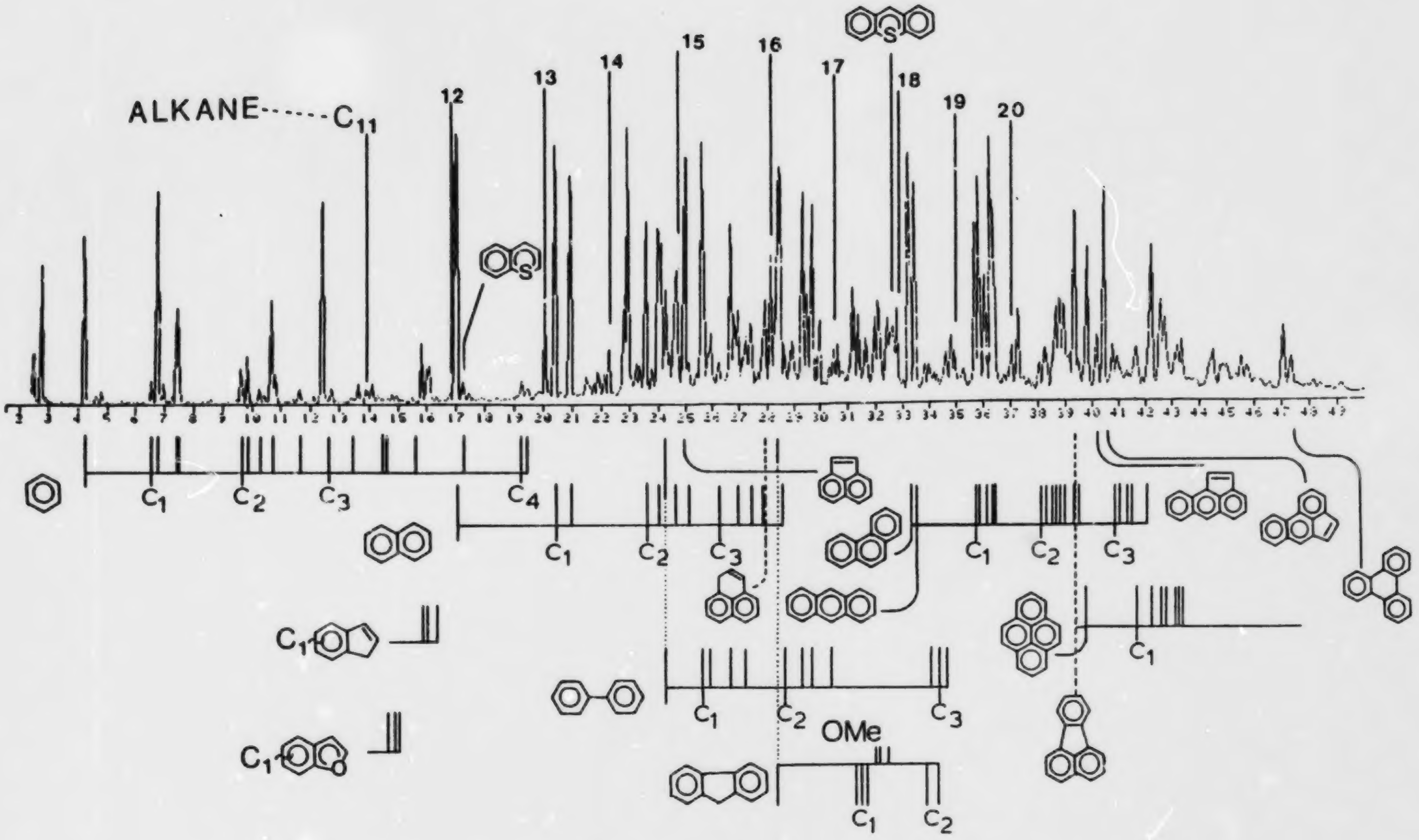


Fig. 10 – Total ion output on GC-MS analysis of Fording hexane soluble fraction (run FC2)

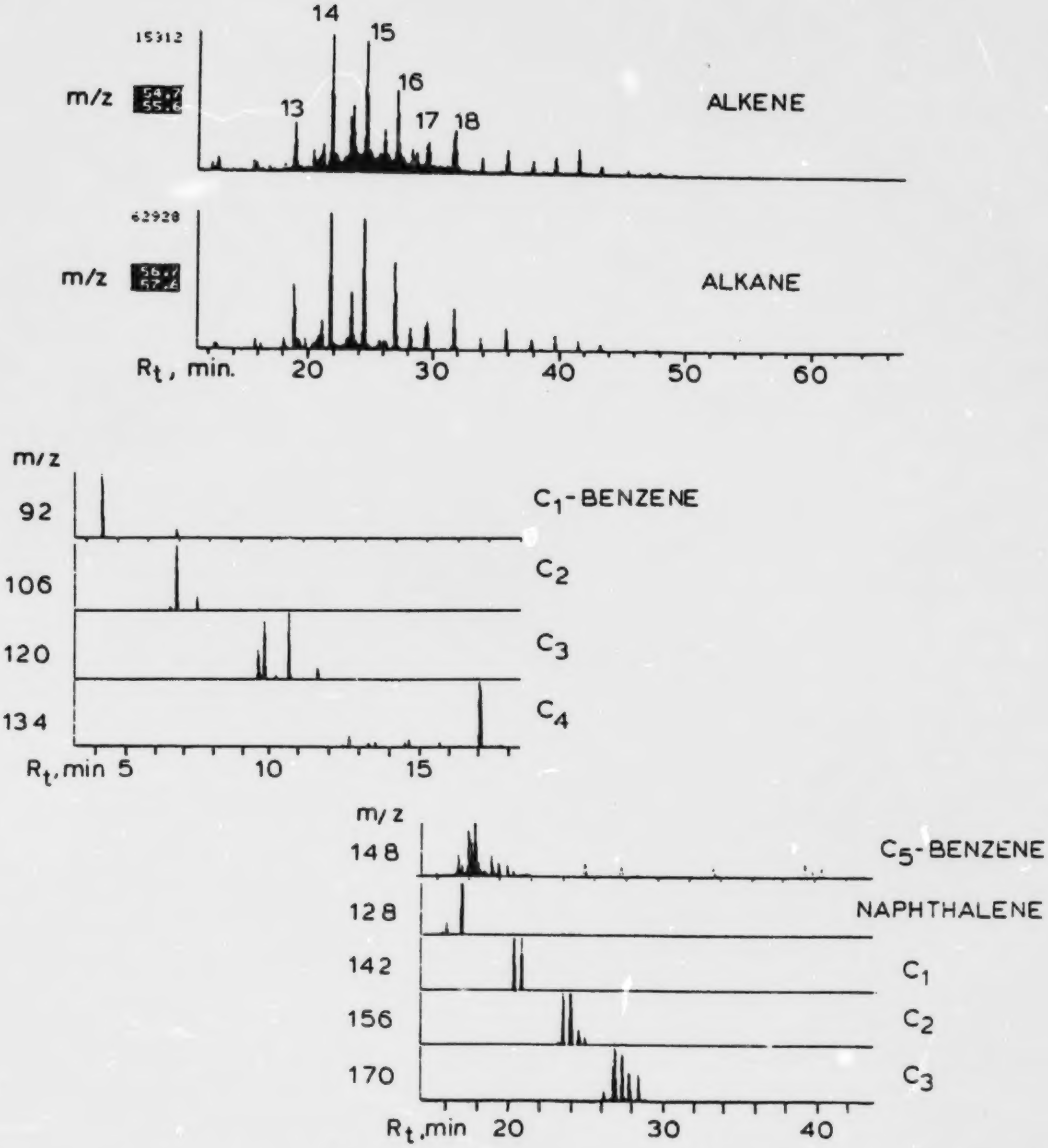


Fig. 11 – Selective ion-monitoring output on GC-MS analysis for alkenes, alkanes, benzenes and naphthalenes from hexane soluble fraction FC2

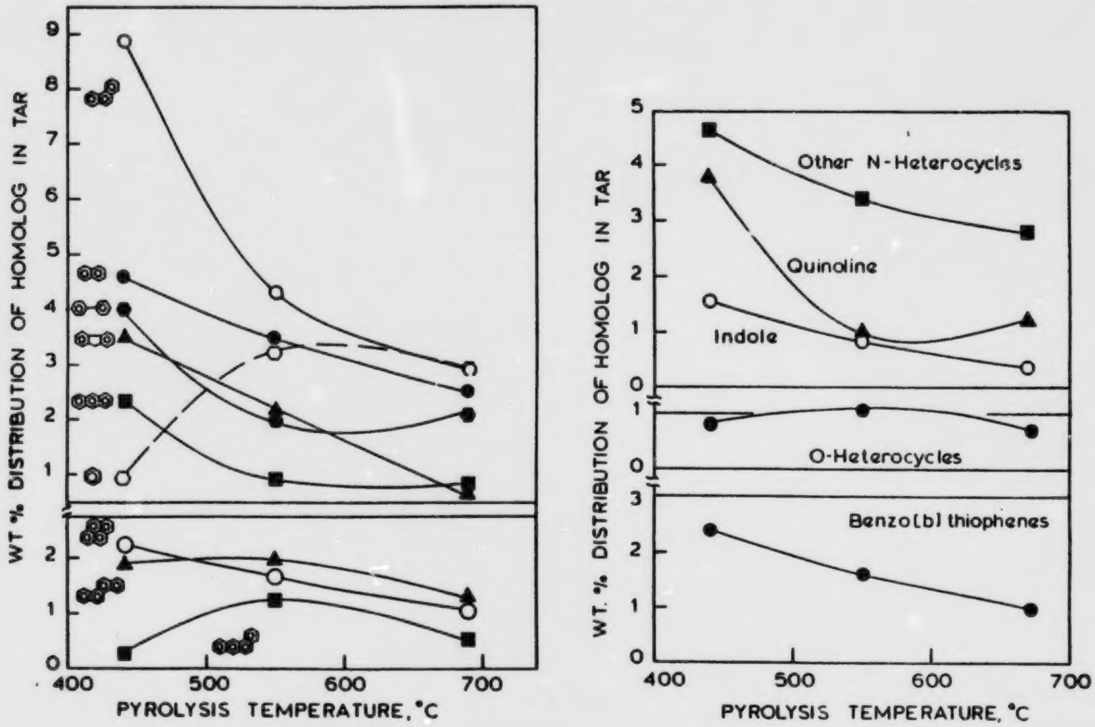


Fig. 12 – Aromatic homolog distribution in hexane + benzene soluble fractions from Devco coal tars

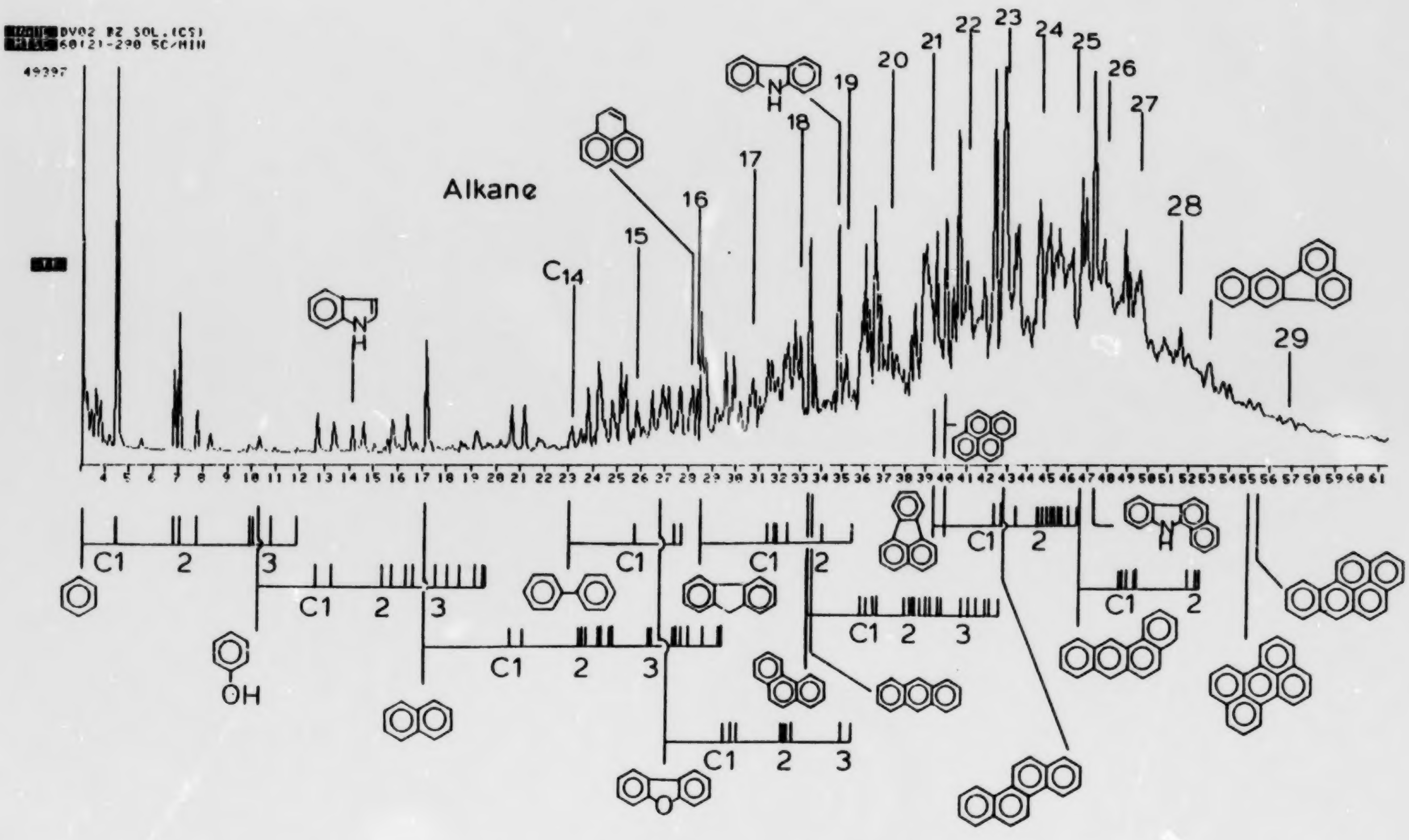


Fig. 13 – Total ion chromatogram of benzene soluble fraction of Devco tar (run DV02)

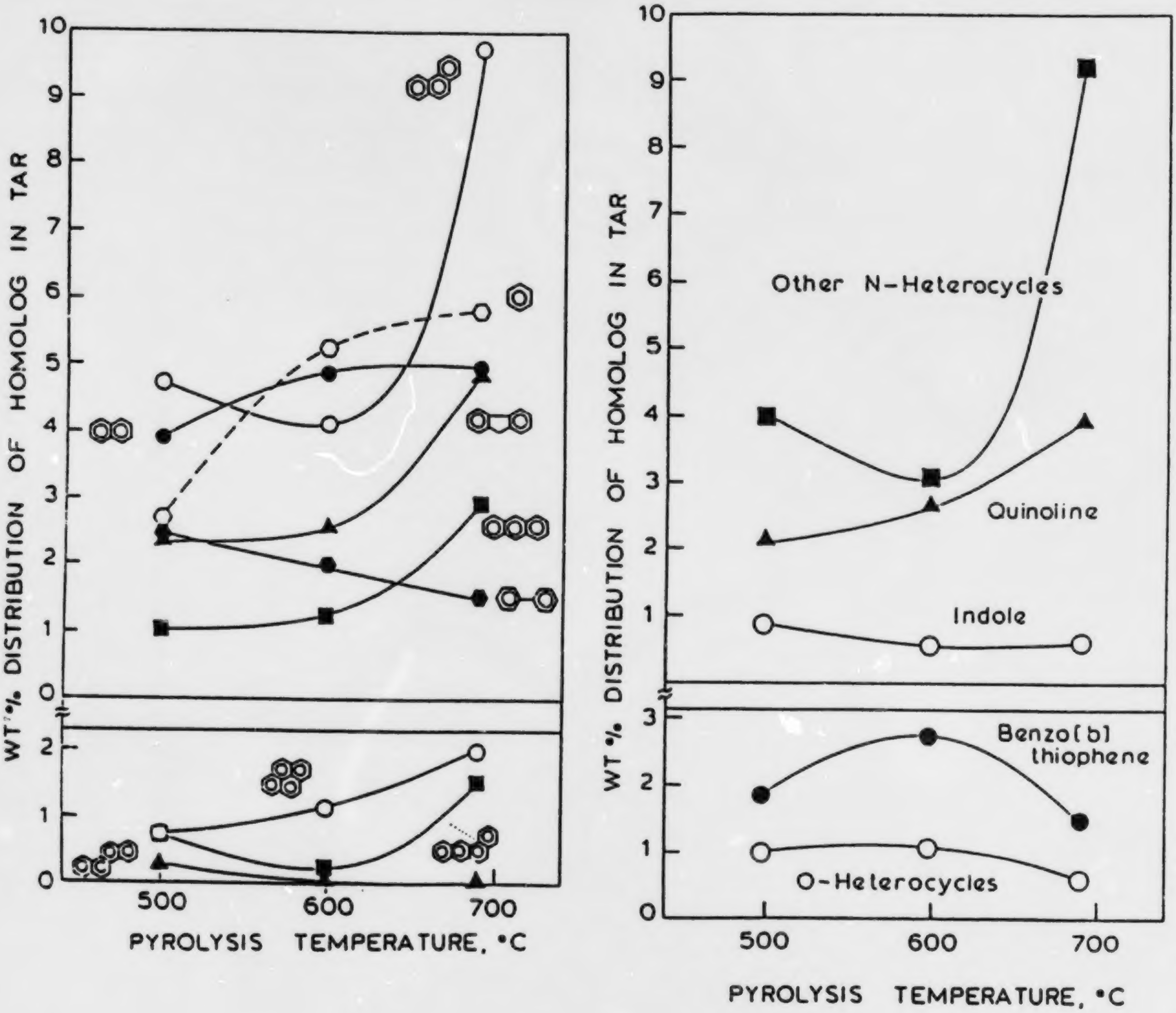


Fig. 14 – Aromatic homolog distribution in hexane + benzene soluble fractions from Minto coal tars

SESSION III: PAPER 12

THE CANMET COAL HYDROPYROLYSIS PROJECT

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ABSTRACT

Pyrolysis and hydropyrolysis are relatively simple methods whereby liquid hydrocarbons may be produced from coal. In order to study these processes on a 1 kg/hr scale, CANMET has had constructed a flash hydropyrolysis unit at the Ontario Research Foundation, Mississauga. The equipment has been used in a short preliminary series of experiments on the hydropyrolysis of Forestburg subbituminous coal. Results from these experiments are discussed, along with plans for future use of the unit.

**denotes speaker*

PRÉSENTATION 12

LE PROJET DE CANMET SUR L'HYDROPYROLYSE DU CHARBON

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RÉSUMÉ

La pyrolyse et l'hydropyrolyse du charbon sont considérées depuis longtemps comme de méthodes relativement simples pour extraire des matières liquides du charbon. Pour étudier les procédés à l'échelle de 1 kg/h, CANMET a fait construire une installation d'hydropyrolyse à l'éclair, à la Fondation de recherche de l'Ontario, à Mississauga et on y a utilisé des charbons sous-bitumineux de Forestburg. La communication présente les résultats de ces expériences et les projets visant l'utilisation future de l'installation.

**indique le conférencier*

THE CANMET COAL HYDROPYROLYSIS PROJECT

INTRODUCTION

Coal pyrolysis has been used for many years for the production of burnable gas, hydrocarbon liquids and coke. More recently, much interest has been shown in rapid or *flash* pyrolysis of coals both in inert atmospheres and in hydrogen. The latter process is usually known as hydropyrolysis. The influence of heating rate on the quantity and quality of products from coal pyrolysis was studied in small-scale apparatus by Squires et al. (1,2) who used U.S. coals, and by Stangeby and Sears in a similar study of Canadian coals (3,4).

The major reason for the slowness in development of flash hydropyrolysis of coal is probably the hydrogen pressure required to achieve worthwhile improvement over straight pyrolysis. A minimum of about 7 MPa hydrogen pressure has been found to be necessary, and this considerably complicates the engineering problems in developing a commercial-scale process. However, if hydropyrolysis can provide a sufficiently attractive product slate, then it will be of interest.

Coal flash pyrolysis processes have been developed up to commercial scale, most notably by Lurgi in Germany and by Occidental and Tosco in the U.S.A. Both the Lurgi and Occidental processes use spent char as the heat carrier for pyrolysis of fresh coal, while in the Tosco *Toscoal* process ceramic balls are used. Yields of volatile material from the coal fed to these processes exceed significantly those expected from Fisher assays. All these processes are quite usable, but interest in their application has waned considerably with the fall in oil prices in the early part of this decade. This situation is unlikely to be permanent though, and when oil prices rise again interest in this type of process is likely to be renewed.

Hydropyrolysis is very much less developed, with work so far restricted to relatively small-scale equipment. Amounts of coal fed are now of the order of a few kilograms per hour, which falls far short of commercial-scale operation. In the U.S.A., Rockwell International, Cities Service Co. and Brookhaven National Laboratory have all worked on about this scale for some years, but similar studies in Canada are only just beginning. Both CANMET and the Alberta Research Council now have equipment similar in basic design to that at the Brookhaven National Laboratory.

The CANMET hydropyrolysis project was begun in 1980 when Kilborn Ltd. of Toronto undertook a contract that involved the construction of a 1 kg/h coal flash hydropyrolysis unit. This unit is now complete and is being operated under contract by Ontario Research Foundation personnel at the premises of O.R.F. in Mississauga.

A preliminary series of hydropyrolysis experiments using Forestburg subbituminous coal has been carried out, and in the light of results from these experiments, procedures for operation of the unit and analysis of the products are being revised in preparation for further work which will begin shortly.

OBJECTIVES

The primary objective of the program is to investigate the processing of Canadian coals in this type of unit. The long-term goal is to develop a process which could be used to *skim off* high-value liquid fuels from coals which are destined for combustion. The opportunity to use a significant fraction of a bituminous coal as liquid fuel or chemical feedstock is now lost when the raw coal is burnt in its entirety. Achievement of this objective is also dependent on the demonstration of reliable burning in a furnace of the char resulting from the pyrolysis or hydropyrolysis process.

THE CANMET FLASH HYDROPYROLYSIS UNIT

The CANMET flash hydropyrolysis unit is based on a heated vertical tubular reactor at the top of which finely divided coal enters and meets preheated hydrogen. Both the coal and the gas flow downwards in the reactor, and at the bottom any solid material falls into a collecting chamber, while gases and vapours pass into a series of condensers. The coal particles in the reactor are in free fall. Figure 1 shows a flow diagram of the unit.

Hydrogen is supplied from cylinders at 6000 psig, and led through pressure and flow regulators into a preheater. Originally, a compressor was built into the system to permit purchase of hydrogen in regular cylinders. However, it proved more practical to use hydrogen which is supplied at high pressure. A helium supply is available for flushing the system.

The gas preheater is of the direct resistance type, where a large current is passed through the tube carrying the gas. In the unit as originally constructed, the tube was heated by a conventional oven, but this proved ineffective and was replaced. The direct resistance method requires the use of an electrical isolator in the line upstream of the heater.

Coal is stored in a pressurized hopper at the top of the reactor tube, and is fed to the reactor by a motor-driven worm feeder at the bottom of the hopper. The rate at which the coal is supplied by this feeder is not as stable as was hoped, and this part of the system is being reconstructed. The bottom section of the hopper system is water cooled to avoid excessive heating of the coal.

Coal fed into the reactor meets the hot hydrogen and flows with it down the reactor. This reactor has an I.D. of 32 mm and a length of 3.7 m. Four ovens maintain the temperature of the top part of the reactor at the required value, which is usually the same as the inlet gas temperature. The lower part of the reactor is not heated, and if necessary may be cooled by passing cold gas through another tube coiled about it. This section of the reactor is used to lower the temperature of the reactants and thus quench the reaction. At intervals down the reactor tube are sample ports to permit sampling of the gas stream at intermediate stages in the reaction. This facility has not been used as yet.

At the bottom of the reactor the char trap collects solid material and the gaseous stream passes into a series of two condensers. The first of these is water cooled and the second is maintained at −70°C by a liquid nitrogen cooling system. These condensers are vertical tubes through which the gases flow from top to bottom, and condensed liquids are collected in traps at the bottoms of each. The remaining gas is vented through a pressure control system and a meter. Samples are taken for analysis.

Because of the dangers involved in the use of high temperatures and high-pressure hydrogen, the unit is equipped with an emergency dump valve, through which the gas may rapidly be vented to the outside. The unit is enclosed in a room which is closed to everyone while a run is in progress, and which is equipped with hydrogen sensors to detect leaks and a ventilation system to remove any hydrogen which does escape.

OPERATION

After the inevitable commissioning problems the unit is now operating smoothly. In spite of the high pressure of gas involved only one point in the system caused significant sealing problems. This was the junction between the low-temperature condenser and its collection trap. On several occasions this junction leaked and subsequently reclosed, leaving no trace of the source of the problem. It was finally realised that this part of the system must be fully cooled before high pressure was applied, to avoid leaks caused by differential contraction of the junction.

In normal operation the feed hopper is loaded with coal, the unit is sealed and then pressurised with helium at 14 MPa. A check is made for leaks, and any that are found are rectified. With a slow flow of helium through the system, the reactor ovens are switched on and the reactor brought up to operating temperature. As the preheater has a very small thermal mass, it is not necessary to switch it on until a few minutes before the start of the run.

When the reactor temperature is near the value required, the helium flow is replaced by hydrogen at the desired flowrate, and the gas preheater is switched on. The temperatures of the reactor and preheater are then allowed to equilibrate while the hydrogen clears the helium from the system. When the situation is stable the coal feeder is switched on.

Two methods of measuring the gas flow are used: the pressure in the hydrogen cylinders and the corresponding time are recorded at approximately six-minute intervals during the run, and the quantity of effluent gas which has left the system is simultaneously noted. A run is defined as the period from the beginning of feed of coal to the end of feed. A mass flowmeter was also included in the hydrogen supply system, but this has so far proven unsatisfactory.

Several samples of effluent gas are taken during the run, but no other product can be collected until the run has ended and the equipment has cooled. The high pressure must be released quite slowly to avoid the loss of volatile material with the gas remaining in the system after the run.

Solid and liquid products are collected and weighed. Analysis of the solid char in the trap at the bottom of the reactor is straightforward, but the liquid in the first condenser trap contains two phases which sometimes tend to form an emulsion. This is not easy to separate. One phase is basically water and the second is a dark, foul-smelling liquid which constitutes the bulk of the hydrocarbon liquid product. The second condenser trap contains a much lighter organic liquid phase without any significant amount of water. The main constituents of this are benzene, toluene and xylenes.

RESULTS AND DISCUSSION

To date, a total of fifteen successful runs have been carried out in the unit. Five of these were the commissioning runs immediately following completion of the unit, and the rest were part of a preliminary contract for its operation. The amount of information gained from each run increased as experience was gained. The primary purpose of the commissioning runs was to achieve acceptable mass balance for the process, so little analytical information was recorded for these. For some of the preliminary contract runs, separation of the water and organic phases from the first trap was not achieved, so the amounts of water and heavy organic material remain unknown. The amounts of lighter aromatic compounds were determined.

Once the type and grind of coal to be used have been decided, four independent variables may be chosen for each run. These are coal feed rate, gas feed rate, pressure and temperature. It is also possible to use different temperatures in different parts of the system, e.g., preheater and main oven, but results from this type of run are of less interest. The residence time of a coal particle in the reactor is dependent on the other variables. An estimate of this may be calculated.

A series of runs were carried out, in each of which only one of the major variables was altered. Of these variables, temperature and pressure could be controlled most accurately. The hydrogen flowrate was set to a value which was calculated to give the desired particle residence time, and the coal feeder motor was driven at a speed which was expected to give the required feedrate. The actual rate could be measured after the event with a fair degree of accuracy, but setting it was only approximate.

The coal used in these experiments was Forestburg subbituminous. Its analysis and particle-size distribution are given in Table 1.

Figure 2 shows the percentage weight loss of the coal on passage through the unit, as a function of temperature in the range 490 to 800°C. Results from experiments carried out at 1000, 1250, 1500 and 1750 psig are shown. The data from experiments at 1000 psig show a smooth curve rising from 15% at 490°C to an apparent maximum of approximately 50% at about 800°C. The effect of higher hydrogen pressure is clearly to increase the weight lost, but it may be seen that the effect is not large and that the data do not permit a detailed assessment of the effect. No account is taken here of the differing coal or hydrogen feedrates used in these experiments.

Figure 3 shows the percentage of carbon in the original coal which was detected as hydrocarbons in the gas product. This shows that conversion of the coal carbon to gas increases both with temperature and with hydrogen pressure. The dependence on pressure is shown more clearly in Figure 4, where the data for 800°C are plotted against pressure.

Significant amounts of carbon are converted to carbon oxides, which also appear in the gas analyses. The total amounts of carbon converted to the oxides are shown in Figure 5. Here it is clear that this parameter has no very strong relationship with either temperature or pressure in the 700 to 800°C range. At 490°C the amount of reaction was so small that virtually no gaseous products were detected.

Yields of benzene, toluene and xylenes were measured for ten runs. These data were plotted against temperature in Figure 6. The scatter in this diagram is quite bad, possibly because of the effects of variations in the flowrates of gas and coal, both of which are not being taken into consideration. Nevertheless, it appears that the yields of BTX are increased by increased pressure and temperature in this range. Significant quantities of naphthalene are also produced, as much as 2% of the coal carbon being converted to this material.

Products which were not adequately separated in this initial study were water and heavy hydrocarbons. From the four runs in which a separation was achieved, indications are that the amount of heavier liquid organic material was from about one to three times the amount of BTX. Separation and analysis of this material is the first objective of the next series of experiments.

The amount of hydrogen in the inlet gas stream is much larger than the amount that reacts with the coal, so the difference between the hydrogen flows in the inlet and outlet streams is relatively small. This makes determination of the overall mass balance for the process somewhat difficult. However, the amount of hydrogen is much smaller than the amounts of other elements, so errors in the hydrogen data are relatively unimportant. The mass of products recovered lies in most cases in the range 95% to 102% of coal reacted. Since some hydrogen has been added, it is clear that product material is being lost, but this is not a very large amount, and the results are quite consistent. There are some indications that the problem is a loss of volatile liquids during system shutdown, and it is hoped that this can be rectified in the next experimental program.

Samples of char resulting from three of the runs were sent for petrographic analysis, with a sample of the original coal for comparison. These runs were carried out using identical hydrogen and coal feedrates and the same hydrogen pressure (1000 psig). The only variable was the temperature, which was 650, 750 and 800°C for the three runs.

Results from the petrographic analyses indicated that the maceral structures of the particles had been completely changed, and that there was no *unaltered coal* at all. This indicates that the particles had been heated throughout during their passage through the reactor. The small amounts of liptinite and inertinite present in the coal had been completely destroyed, leaving just the huminite macerals. The huminite macerals were converted to vesicular material, which was classified at the analysing laboratory into *vesicular* and *high vesicular* categories. It was noted that the proportion of the latter rose markedly with reaction temperature. Reflectance measurements showed that the mean reflectance of the coal rose on hydropyrolysis and rose further with increasing temperature.

The residence time of the coal particle in the reactor depends on all the reaction conditions except coal feedrate. A figure can be calculated for a particle of any given diameter by assuming free fall in the moving gas in the reactor. However, the coal used in these experiments was not of completely uniform size, and the smaller particles have longer residence times, which results in more complete reaction for them. Particle-size analysis on the coal and chars indicates that the smaller particles do indeed lose more material than do the large ones, thus becoming still smaller and slower falling. This situation can result in complete disappearance of the smallest particles. Care is required in the interpretation of calculated particle residence times.

CONCLUSIONS

The CANMET hydropyrolysis unit has shown itself to be a reliable piece of equipment which is quite straightforward to operate. Problems remain to be solved, the major ones being product recovery and workup, but the unit may now be run on a routine basis. The results obtained so far are consistent with those from earlier small-scale work and show that quite substantial yields of liquid products can be obtained. It is important now to develop methods whereby the heavier liquid products may be characterized, and then to optimize production of useful liquid while minimizing the amount of hydrogen which is used in the formation of gaseous hydrocarbons.

High-volatile bituminous coals will be processed in the unit, as these may be expected to provide the best yields of liquid products. This will require solutions to the problem of caking which can easily occur with these coals.

Finally, if conditions can be found which provide a good product slate, it will be necessary to develop a process for the hydropyrolysis of larger quantities of coal. This will present new difficulties, a major one being the transfer of heat to reactants in a large reactor vessel. This stage of development is still some way off.

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TABLE

Table 1 – Coal analysis

Component	Weight per cent
Fixed carbon	48.14 mf
Volatiles	39.87 mf
Ash	11.99 mf
Moisture	2.36
Carbon	67.96 maf
Hydrogen	4.91 maf
Oxygen	25.69 maf
Nitrogen	1.19 maf
Sulphur	0.25 maf
Size range (um)	**Weight per cent**
>297	3.7
210-297	24.5
177-210	32.2
149-177	15.8
105-149	18.8
<105	4.9

FIGURES

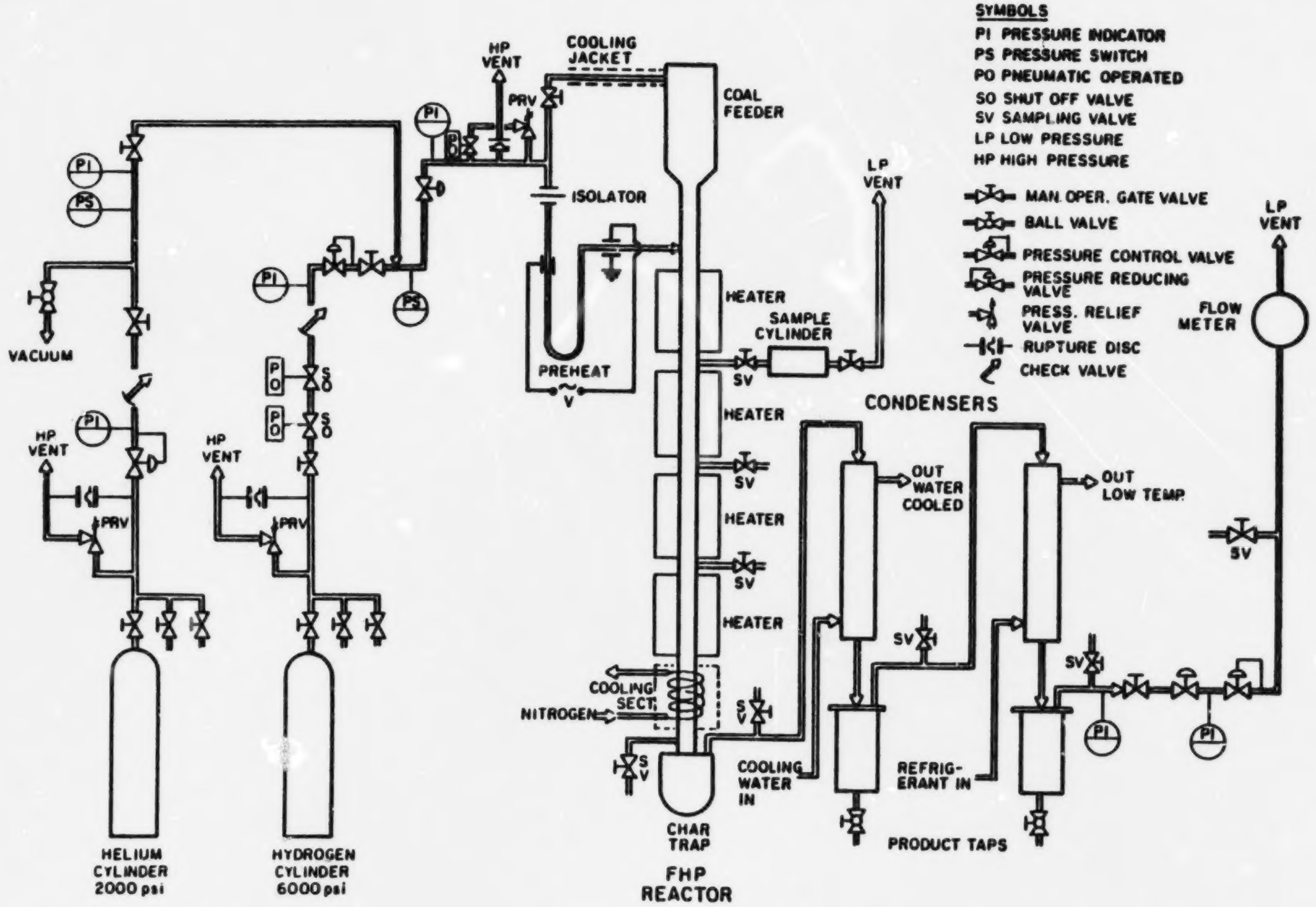
SYMBOLS
PI PRESSURE INDICATOR
PS PRESSURE SWITCH
PO PNEUMATIC OPERATED
SO SHUT OFF VALVE
SV SAMPLING VALVE
LP LOW PRESSURE
HP HIGH PRESSURE
MAN. OPER. GATE VALVE
BALL VALVE
PRESSURE CONTROL VALVE
PRESSURE REDUCING VALVE
PRESS. RELIEF VALVE
RUPTURE DISC
CHECK VALVE
HP VENT
COOLING JACKET
PRV
PI
PS
VACUUM
ISOLATOR
COAL FEEDER
LP VENT
HEATER
SAMPLE CYLINDER
SV
PREHEAT
V
P O
S O
CONDENSERS
OUT WATER COOLED
OUT LOW TEMP.
FLOW METER
LP VENT
COOLING SECT.
NITROGEN
COOLING WATER IN
REFRIG-ERANT IN
PRODUCT TAPS
CHAR TRAP
FHP REACTOR
HELIUM CYLINDER 2000 psi
HYDROGEN CYLINDER 6000 psi

Fig. 1 – CANMET and Ontario Research Foundation process flow diagram - flash hydropyrolysis pilot unit

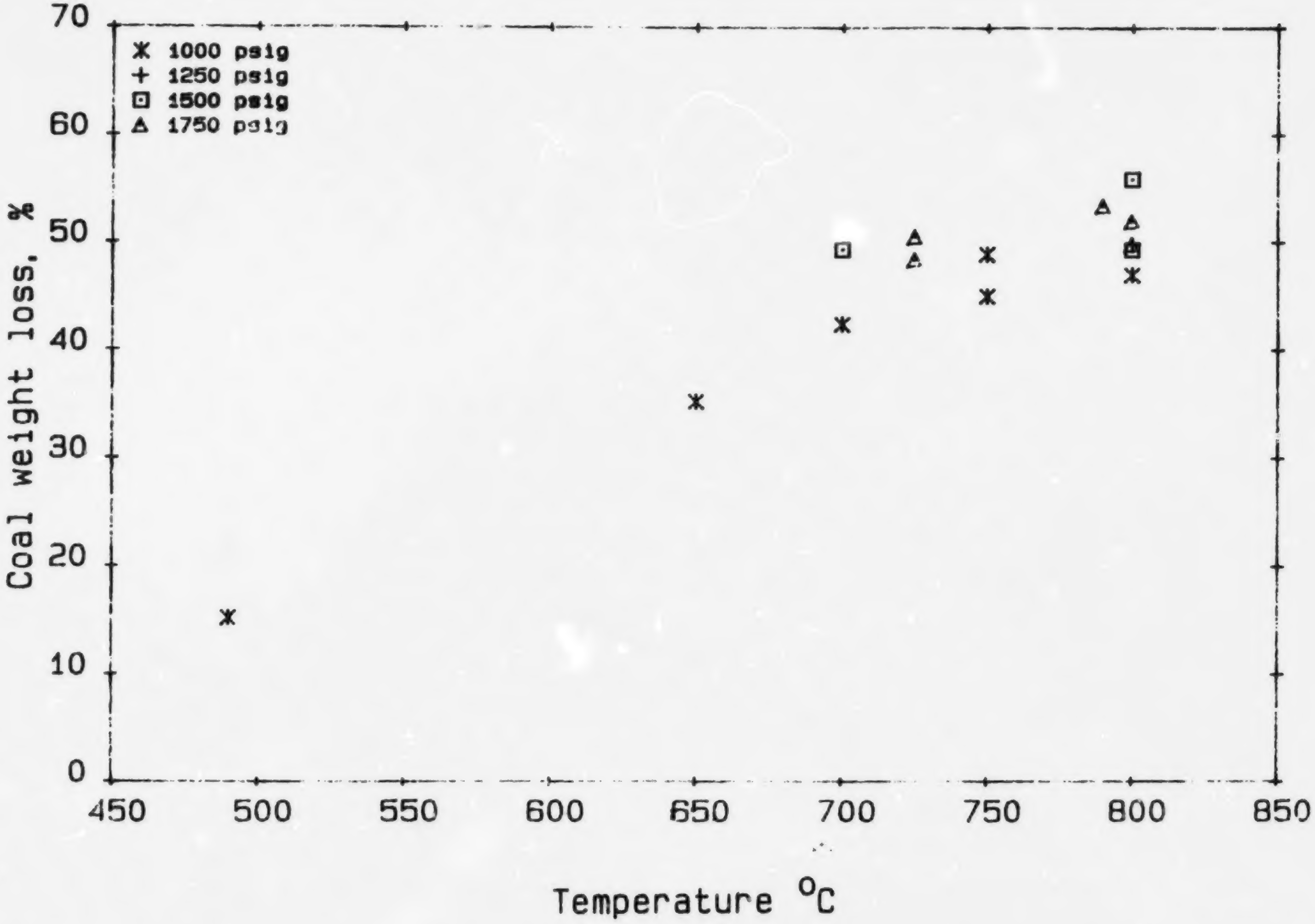

Fig. 2 – Coal weight loss, temperature dependence

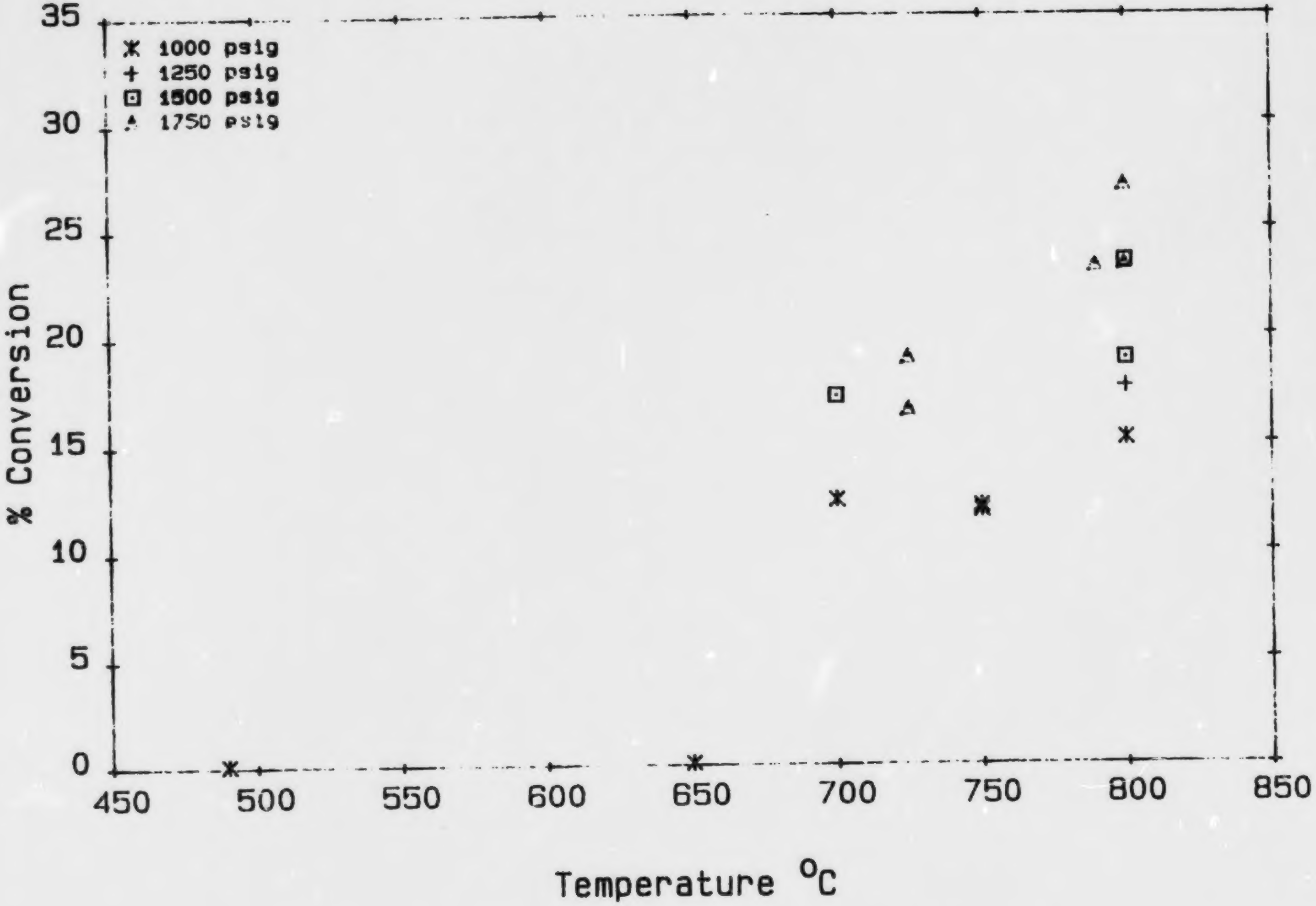

Fig. 3 – Coal carbon converted to hydrocarbon gas, temperature dependence

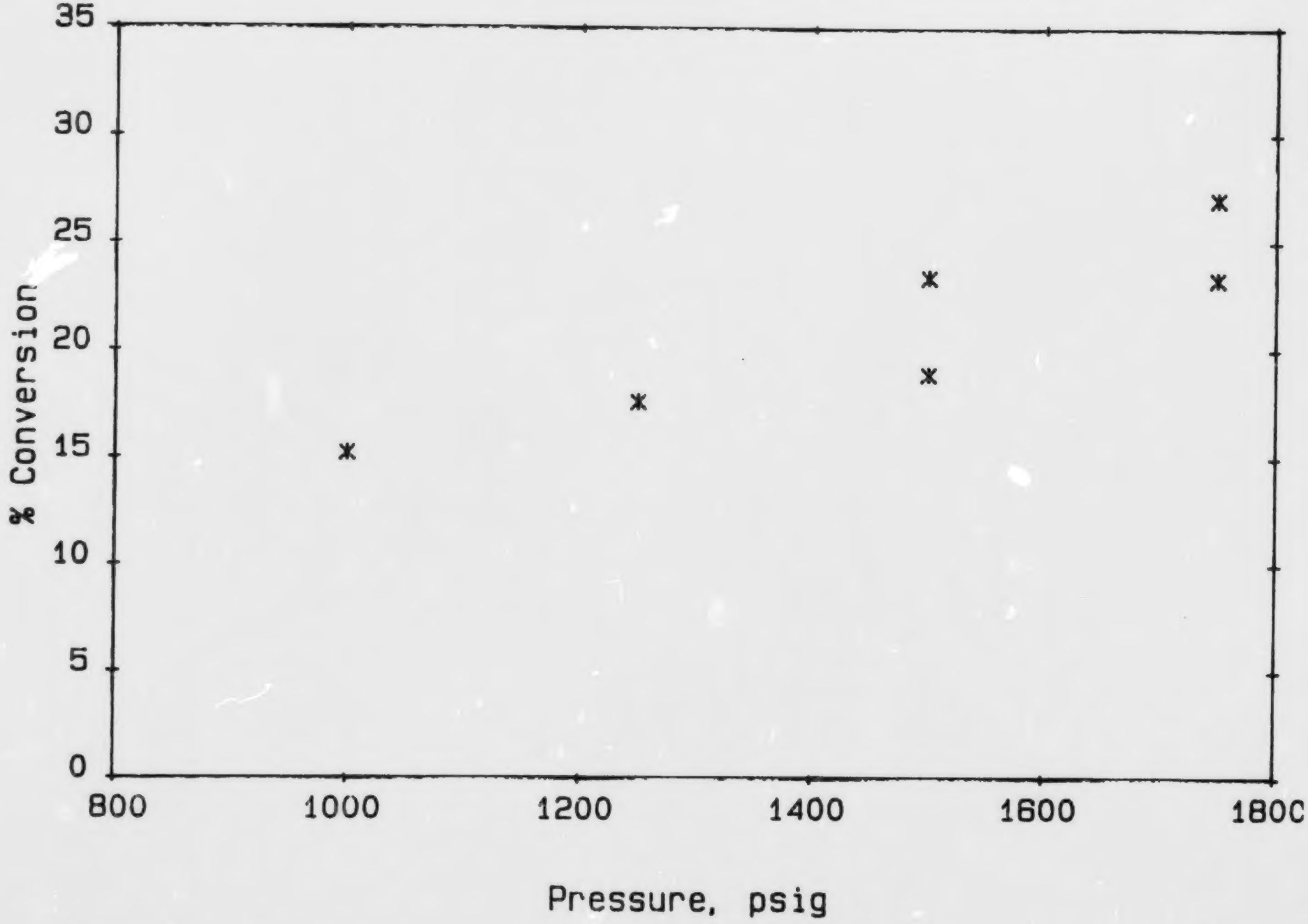

Fig. 4 – Coal carbon converted to hydrocarbon gas, pressure dependence at 800°C

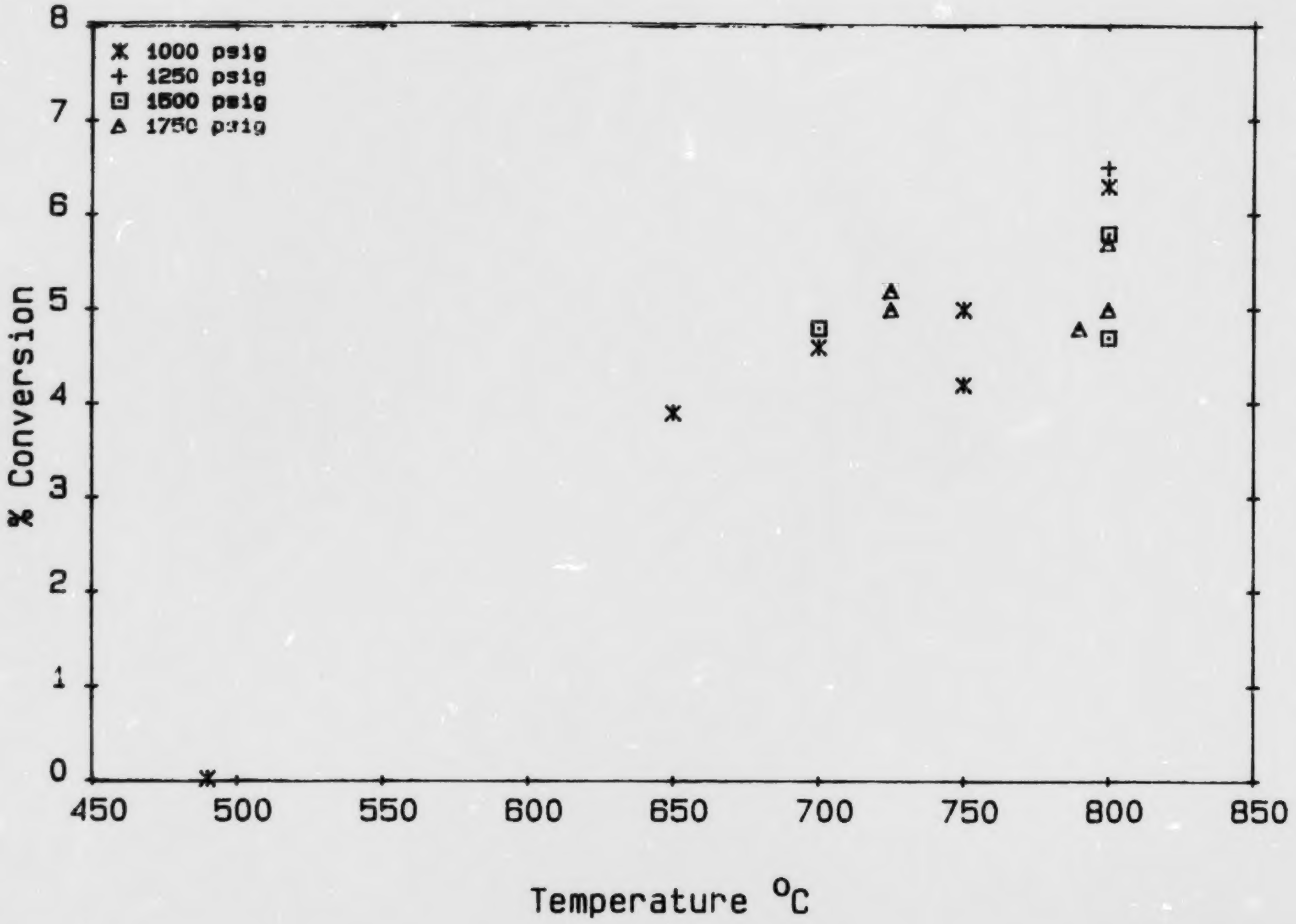

Fig. 5 – Coal carbon converted to CO and CO_2, temperature dependence

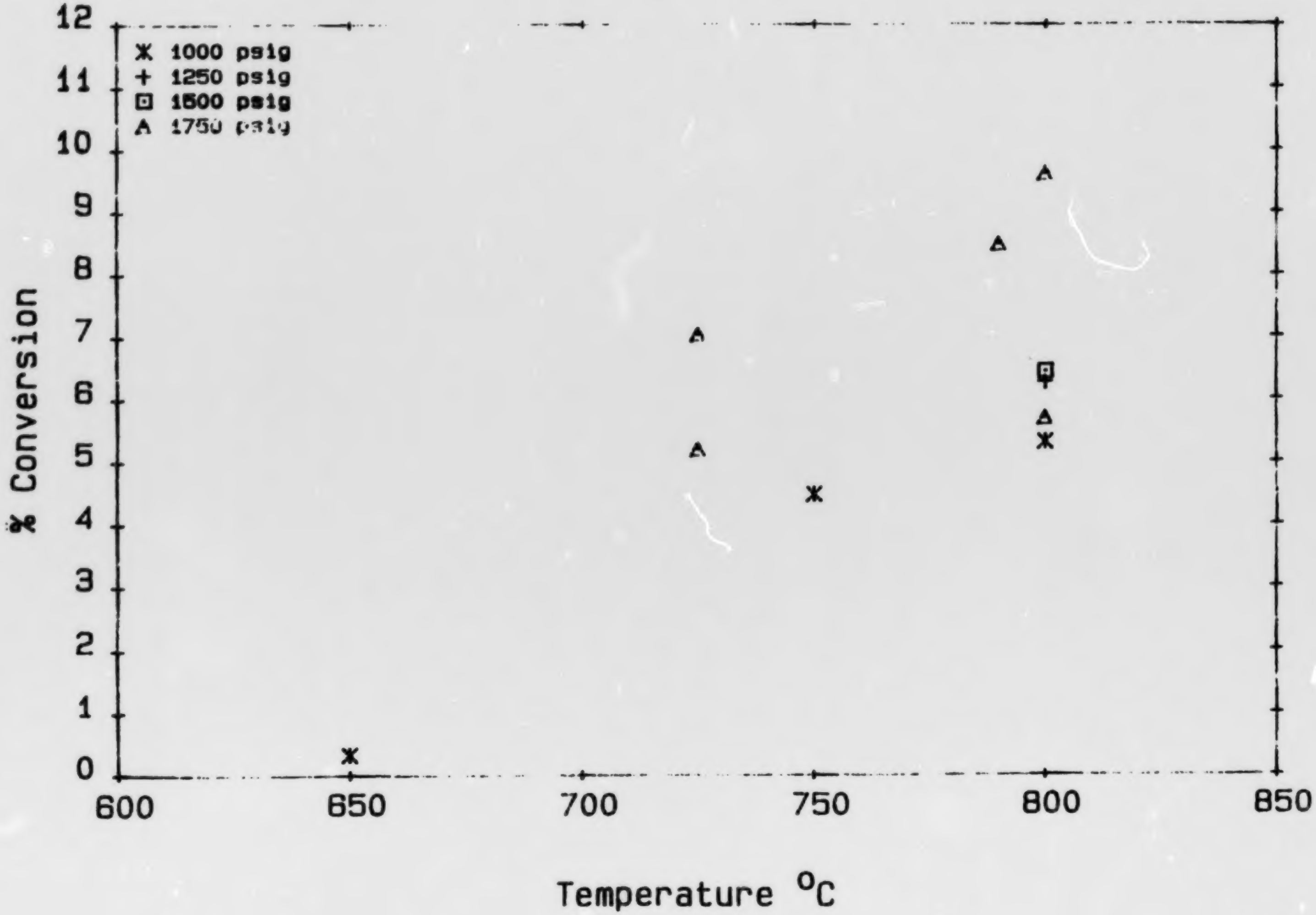

Fig. 6 – Coal carbon converted to BTX, temperature dependence

SESSION III: PAPER 13

THE CHARACTERIZATION OF COAL LIQUEFACTION FEEDSTOCKS AND RESIDUES BY PETROGRAPHIC ANALYSIS

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ABSTRACT

Reflected light, optical microscopy has been used to study coal feedstocks and the solid products of coal/bitumen coprocessing, spouted-bed pyrolysis, flash hydropyrolysis and low-temperature liquefaction. The coal feedstocks were characterized by the maceral composition and the reflectance of the vitrinite/huminite components. The solid products were characterized by the unaltered coal, altered coal, and highly altered coal constituents and the bituminous components; they were further classified on the basis of optical character, as *non-liquefiable* (inerts, semicoke, coke and char) and *liquefiable* products (coal-derived and bituminous solids). The effects of variable operating conditions on the composition of the residues, were also demonstrated.

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*denotes speaker

PRÉSENTATION 13

DÉTERMINATION DES CARACTÉRISTIQUES DES MATIÈRES PREMIÈRES ET DES RÉSIDUS SOLIDES DE LIQUÉFACTION DU CHARBON PAR L'ANALYSE PÉTROGRAPHIQUE

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RÉSUMÉ

Le Groupe de recherche sur le charbon a utilisé la microscopie optique à lumière réfléchie pour étudier les matières premières et les produits solides dérivés du co-traitement du charbon et du bitume, de la pyrolyse sur lit à jet, de l'hydropyrolyse éclair et de la liquéfaction à basse température. Les matières premières ont été caractérisées par la composition macérale et la reflectance des composés vitrinite-huminite. Les produits solides ont été caractérisés par le charbon non altéré, le charbon altéré et les composés de charbon très altérés et les composés bitumineux; ils ont de plus été classés d'après leur caractère optique comme produits non liquéfiables (matière inerte, semi-coke, coke et produits de carbonisation) et produits liquéfiables (dérivés du charbon et solides bitumineux). On a également démontré les effets de conditions de marche variables sur la composition des résidus.

**indique le conférencier*

THE CHARACTERIZATION OF COAL LIQUEFACTION FEEDSTOCKS AND RESIDUES BY PETROGRAPHIC ANALYSIS

INTRODUCTION

The Coal Research Group at the University of Regina has used reflected light optical microscopy to study coal feedstocks, product residues and distillation residues from coal conversion processes. These studies, which began in 1980, have been largely funded by Energy, Mines and Resources Canada, through the CANMET coal liquefaction program. Samples generated from a variety of 'in-house' studies at the Energy Research Laboratories, CANMET and by numerous CANMET coal conversion contractors, have been examined and characterized during the course of this work.

Standard terminology, (International Committee for Coal Petrology, I.C.C.P.; 1965, 1975) is applied to the microscopical components of a variety of coal feedstocks ranging from lignites to high-volatile bituminous coals. It was necessary to develop terminology for the residue components which was both meaningful to coal conversion technologists and applicable to various coal conversion processes ranging from low-temperature liquefaction to pyrolysis, and from coal conversion to coal/oil and coal/bitumen coprocessing.

In this paper we would like to report on some of the petrographic characteristics of the Canadian coal feedstocks and solid products from (1) flash hydropyrolysis; (2) spouted-bed pyrolysis; (3) liquefaction at low temperatures using long residence times; and (4) coal/bitumen coprocessing using H_2S/H_2, that were investigated under DSS Contract No. OSU83-00127 (Energy Research Unit, 1984). In doing so we would like to address the following applications of organic petrography to coal conversion studies:

- variations in coal type and rank that affect the liquefaction potential
- variations in the characters of the solid residues that affect liquid yields (unaltered coal, partially liquefied coal, coal char, semicoke and coke)
- identification of coal-derived and bitumen-derived solids in the residues from coal/bitumen coprocessing
- the effects of variable operating conditions.

TERMINOLOGY

Coal feedstocks

Coal feedstocks are assessed according to coal rank and coal type. Rank determinations are based on vitrinite/huminite reflectance (in this case R_O random) measurements, obtained by standard petrographic procedures (I.C.C.P., 1965). Correlations between vitrinite reflectance and other rank parameters for high-rank coals have already been made (van Krevelen, 1981) but reliable relationships have not yet been established for low-rank coals. Nevertheless, huminite reflectance is employed as an approximate rank indicator for coals of lignite and subbituminous rank. It is particularly useful in coal liquefaction studies for measuring relative chemical differences between coal macerals and their solid products.

Coal type refers to the petrographic composition of the coal which is expressed in terms of the relative abundance of coal macerals. The International Committee for Coal Petrology recognises two classifications for coal macerals: one for brown coals (lignites and subbituminous) and another for hard coals (bituminous). A simplified, combined classification and some of the optical properties are shown in Table 1. The dominant constituents of low-rank coals are the *huminites*; these are reactive macerals which on geochemical maturation would normally become the *vitrinites* of higher ranking coals. The *liptinite group* comprises very reactive macerals with high H/C ratios; they alter very gradually during the coalification process and are the precursors of the *exinite* macerals in hard coals. *Inertinites* are inert or semi-inert macerals which can exist in all ranks of coal. Inertinites is a petrographic term for macerals derived by oxidation of vegetal materials; they are not necessarily chemically unreactive. *Mineral matter* is usually included in coal-type analysis; this term applies only to identifiable crystalline, inorganic minerals that are inherent in the coal. Some of the more common minerals are included in Table 1.

Solid Products

Numerous approaches towards a petrographic classification for the components of coal liquefaction residues have been documented during the last decade (Guyot and Diessel, 1979; Given et al., 1975; Shiboaka and Ueda, 1978;

Mitchell et al., 1977; Ng, 1982). Currently, a coal liquefaction residue working group of the International Committee for Coal Petrology is addressing the problem of standardizing the terminology. Most of the terminology in the literature was developed for coal hydrogenation residues and, more recently, for solvent-refined coals of bituminous rank. Most of our work has been with low-rank Canadian coals; viz. lignites, subbituminous and high-volatile bituminous coals, and their products from hydroliquefaction, pyrolysis and coal/bitumen coprocessing. We have tried, therefore, to establish a classification for the residual solids that can be applied to all types of coal liquefaction residues. This classification is given in Table 2. The 'essential' components of this system are: *unaltered coal, altered coal* and *mineral matter*. Additionally, *bituminous solids* and *highly altered coal* may be present, depending upon the liquefaction process used.

The objectives of a residue classification of this sort are to characterize the components according to optical characters and to give an indication of their origin. This is particularly important to the study of coal/oil and coal/bitumen coprocessing residues where the proportion of coal-derived solids in the residue is critical to coal conversion calculations. For these reasons, the authors have avoided the use of specialized terms which describe only the optical and morphological characters of the components. In some cases, however, this is unavoidable. For example, we use the term *vitroplast* originally introduced by Mitchell et al. (1977) for particles with a spherical morphology. Synonymous terms such as *coagulant* were preferred by Diessel and Guyot (1979), because they have no genetic implications. In this classification (Table 2), vitroplast is an appropriate term pertaining only to spherical particles derived from vitrinite/huminite. The terminology and definitions of residue components that we recognize as derivatives of coal macerals, agree well with those used by Whitehurst et al. (1980) and by Ng (1982).

Unaltered coal

This group comprises inertinites, vitrinites/huminites and exinites/liptinites resembling the macerals in the feed coal, i.e., with no alteration to the reflectance or the morphology.

Altered coal

This group comprises reacted and partially reacted coal, specifically inertinites which have an increased reflectivity and a variety of morphologically altered, vitrinite/huminite derivatives. Those which are isotropic have apparently undergone some liquefaction and, depending upon the reflectivity, are still potentially liquefiable. These are: (i) isotropic char: a solid product which may be rounded and vesicular indicating emission of volatile components, or angular fragments with no signs of softening or devolatilization; (ii) isotropic vitroplast: spherules of softened vitrinite/huminite or remnants of liquefied vitrinite/huminite; (iii) isotropic granular residue: the unliquefied remains of *groundmass* vitrinite/huminite which is intimately associated with finely divided mineral matter (see Terminology) and is partially soluble in pentane and toluene.

The anisotropic components are insoluble and optically anisotropic semicokes which result from mild carbonization of isotropic vitrinites/huminites and, occasionally, inertinites. Destruction of cross linkages between *carbon layers* enhances mobility of the layers, which reorder producing non-graphitic, non-liquefiable, semicoke. Most commonly they display mosaic textures.

Highly altered coal

This is the dominant product of coal pyrolysis. The isotropic form is a highly reflecting (R_o >3.0%) vitrinitic/huminitic/inertinitic char which may be vesicular, indicating emission of gaseous products. The optically anisotropic component is similar to that produced by coal carbonization, i.e., high-temperature coke which is non-liquefiable.

Bituminous solids

These are weakly reflecting, bitumen-like components which exhibit reflectivities lower than those of the isotropic vitrinite/huminite in the same residue and those of the feed coal. They are either the intermediate products of coal liquefaction or they derive from coprocessing agents such as heavy oils or bitumens. The isotropic forms commonly occur as (i) rounded, vesicular particles and; (ii) *bituplast*: spherules or agglomerations of small spherules, which morphologically resemble vitroplast from coal macerals but have a lower reflectance; all are considered to be capable of further liquefaction.

The anisotropic components in this group develop from the isotropic form via coalescence of optically anisotropic mesophase spherules. This gives rise to variously textured semicokes; these are non-liquefiable, non-graphitic, mosaic or flow-textured solids.

Mineral Matter

Our attentions have been focused on the organic components of the residues and not to any significant degree on the inorganic components. However, it has been noted that iron sulphides (pyrite/marcasite) commonly alter to pyrrhotite and that fine sub-micron sized, clay mineral-like particles form an essential part of the granular residue (and semicoke that forms from it) in the altered coal. It is particularly abundant in tetrahydrofurane insoluble residues.

Flash Hydropyrolysis

A sample of Forestburg coal and three product residues from flash hydropyrolysis experiments run at different temperatures were characterized petrographically.

Coal feedstock

According to its reflectance ($R_O = 0.49\%$), the coal feedstock is a subbituminous coal; typically it is a huminite-rich coal (89.9%) containing minor amounts of liptinite (3.6%) and inertinite (5.4%) macerals, and very little mineral matter (1.2%). The huminites are dominantly structured macerals (61.2%); groundmass (densinite) makes up 19.4% and unstructured macerals, 9.2% (Table 3).

Residues

The reflectance of the residues varies between 1.46% and 2.45%; it increases with the pyrolysis temperature (Fig. 1) indicating that the residues are more carbonaceous at elevated temperatures. The reflectance also indicates that the products of Forestburg coal comprise altered (i.e. reacted) coal.

The products from flash hydropyrolysis of Forestburg coal are also optically isotropic residues (Table 4); no anisotropic solids (semicokes) were observed.

The altered coal products are principally derivatives of huminite macerals with minor inertinite fractions (1.2-4.2%); remnants of liptinite macerals are absent indicating total liquefaction. The residues contain fewer inertinites than the coal feedstock, suggesting that the majority of them are reactive under hydropyrolysis conditions. The huminitic residues were further characterized according to the presence and extent of vesiculation developed (Table 4). Vesicules are pores or irregular holes in the residue particles which reflect the physical alteration of the coal maceral when gaseous products are emitted. The type and extent of vesiculation exhibited by these residues appears to be controlled by maceral type and pyrolysis conditions (Fig. 2). The highly vesicular chars are the products of extensive devolatilisation of the structured huminites. These are more abundant at higher temperatures, suggesting that more gaseous products were obtained at higher pyrolysis temperatures. Indeed the high-temperature products closely resemble the residues produced by coal gasification; the chars produced at lower temperature are more reminiscent of hydrogenation products.

Spouted-bed Pyrolysis

Three coal feedstocks (Forestburg, Onakawana and Fordings) and thirteen product residues from spouted-bed pyrolysis experiments, run at variable temperatures, were characterized.

Coal feedstocks

Variations in the vitrinite/huminite reflectance of the coal feedstocks indicate marked differences in the coal ranks (Table 5). The Forestburg coal is subbituminous; the Fordings coal is a high-volatile bituminous coal; and the Onakawana coal is an immature lignite which would be classified as soft brown coal in Europe.

The Forestburg samples are huminite rich, with minor amounts of liptinites (3.8% av. and 3.2%) and inertinite macerals (5.6% av. and 5.0%) and very little mineral matter (1.4% av. and 1.8%; Table 5). Despite their vast differences in rank the Fordings and Onakawana coals are typologically similar; each has a significantly high inertinite content (22.0% and 18.3%), very little liptinite (1.0% and 3.7%) and fairly similar vitrinite/huminite contents (75.2% – and 73.2%).

Residues

The solid products of spouted-bed pyrolysis are: unaltered coal, altered coal, highly altered coal and mineral matter; the relative abundances of each are shown in Table 6. The lower rank coals are the only ones to produce unaltered coal; this comprises vitrinite/huminite and inertinite macerals. In the Forestburg it is a minor constituent (up to 2.2%); in the Onakawana residues it is a major constituent (15%), particularly in the products of lower temperature pyrolysis (Fig. 3).

The dominant component in all residues is reacted or partially reacted coal (Table 6) mostly derived from vitrinite/huminites. Some of this altered coal is anisotropic semicoke. Small but significant amounts (generally less than 4.0%) of semicoke occur in the products of the Forestburg and Onakawana coals. In the Fordings residues, reacted anisotropic semicoke constitutes 16% to 32% of the total product. There is no direct relationship between the formation of semicoke and the pyrolysis temperature; rather it is related to the rank of the coal feedstock, as indicated by the reflectance of the coal (Fig. 4).

Highly altered components were found only in the Fordings residues. They comprise a highly reflecting isotropic char (which varies from 11% to 18.6% of the total product) and a significantly large amount of high-temperature coke (15.4% to 20.4%). These components do not occur in any of the other chars and therefore can probably be attributed to the rank/type of the Fordings coal.

The reflectance of the reacted vitrinites/huminites in the solid residues are also given in Table 6. The relationship between the reflectance (R_O random) and the pyrolysis temperature is shown in Figure 5. The level of alteration of the vitrinites/huminites in the low-rank coals, as indicated by the reflectance, increases as the pyrolysis temperature increases. The Fordings coal produced a poorly reacted product, in which the reflectance was only slightly greater than the feed coal, and a highly reacted product, with exceptionally high reflectance, comprising coke and coal char. It is our opinion that the char and coke form because of the coal type (the high inertinite content may have promoted coking of associated vitrinite) and the rank (high-volatile bituminous). In more conventional liquefaction processes, coals like the Fordings coal with reflectivities greater than 0.8% R_O random are more susceptible to coking than lower rank coals.

LOW-TEMPERATURE LIQUEFACTION

Estevan lignite and five products from long residence time/low-temperature hydrogenation experiments were characterized.

Feedstock

This sample of Estevan lignite is inertinite rich (19.8%) and contains small amounts of liptinite macerals (4.8%) which, because of the high H/C ratios, are desirable in a liquefaction feed coal. The major constituents are huminites; predominantly, these are structured macerals with good liquefaction potential (Table 7). The reflectance is 0.35% R_O random, indicating a lignite coal.

Residues

The liquefaction residues comprise unalerted coal, altered coal and mineral matter; no residual solids from solvents were observed (Table 8). The unaltered coal comprises inertinites only (0.4-4.8%), indicating that all the reactive macerals (huminites and liptinites) and quite obviously most of the inertinite macerals reacted.

The altered coal is derived from huminites and inertinites; the solid products are optically isotropic (71.2-91.6%) and anisotropic semicokes (2.0-27.2%). Mineral matter is a minor constituent (Table 8). The reflectance values obtained for the isotropic solids (Table 8) range from 0.85% to 1.48%. The higher the value the greater the chemical changes in the huminitic solids, due to the removal of liquid and gaseous products. The highest values were obtained at higher temperatures. Residues with values lower than 1.3% are probably still liquefiable (under natural thermal maturation conditions, coaly kerogens are considered to produce natural petroleum up to the 1.3% mark).

Much of the altered coal comprises a granular solid product intimately associated with finely dispersed, sub-micron-sized minerals. This is the principal product of huminite liquefaction. It ranges from 14.6% to 67.8% of the residues, and as shown in Figure 6, there is good agreement between the amount of granular residue and calculated coal conversion. The best conversions were attained in the production of residues 9 and 10, and yet residue 4 contained the most granular residue. This is because residues 9 and 10 contain very little anisotropic semicoke (Table 8; 2.0%), and residue 4 contains 27.2% semicoke which formed in the granular residue. Characteristically, semicoke is produced during coal liquefaction at high temperatures; it is an insoluble product which is incapable of further liquefaction.

COAL/BITUMEN COPROCESSING

The role of hydrogen sulphide in preventing semicoke formation in the solid products from the coprocessing of Forestburg coal with Cold Lake vacuum bottom oil was investigated petrographically.

Feedstocks

The petrographic composition of two samples of the Forestburg feedstock is given in Table 9. It is a huminite-rich coal (92.2% – 94.8%) with minor small amounts of liptinite (2.9%, 2.4%) and inertinite macerals (4.2%, 3.0%). Most of the huminites are reactive structured macerals (71.8%, 75.2%) which makes the coal composition favourable for coal liquefaction. The reflectance of the huminite (0.4%) indicates that the coal is subbituminous.

Residues

With residues from coal/bitumen coprocessing it is necessary to identify solids derived from the Cold Lake vacuum bottom oil as well as unaltered coal and altered coal. This is more easily achieved when the products are anisotropic. The isotropic products from the bitumen often resemble the intermediate products of coal liquefaction, which are probably asphaltenes and preasphaltenes. In the residues examined, the optical and morphological properties of the isotropic solids generated by processing the vacuum bottom oil without coal are identified with the bituminous products of coal/oil coprocessing. We believe, therefore, that in this case the isotropic solids derive entirely from the Cold Lake bitumen.

Table 10 shows the relative abundance of coal versus bitumen-derived solids in eighteen residues from Forestburg coal-Cold Lake vacuum bottom oil coprocessing.

Additionally, the relative abundance of isotropic versus anistropic (semicoke) solids was determined (Table 11). These values represent the sum of the isotropic solids, and the sum of the anisotropic solids or semicoke, from the coal and the oil. In Figure 7 the percentage of anisotropic solids (toluene insoluble semicoke) is plotted against the concentration of H_2S in the hydrogen atmosphere. Residues generated under similar experimental conditions are given the same symbol; the residues generated by coal/oil coprocessing in hydrogen are represented by open symbols, while those generated under corresponding conditions in H_2S/H_2 are represented by solid symbols. With the exception of one pair of residues (105 and 106), there is less semicoke in residues generated in the presence of H_2S. Pairs of residues generated under similar experimental conditions, but at relatively low-temperatures, exhibit smaller differences in the semicoke content. Residues which contain large amounts of semicoke were generated at relatively high-temperatures; the difference between the semicoke contents is also much more pronounced. This suggests that H_2S is indeed effective in preventing or delaying semicoke formation in the product residues from coal/oil coprocessing, particularly at elevated temperatures when it is most likely to form in abundance.

CONCLUSIONS

1. The solid products from flash hydropyrolysis of Forestburg coal comprise altered or reacted coal derived principally from huminite macerals. Semi-inert macerals also appear to respond favourably to this type of coal liquefaction.
2. The residues from flash hydropyrolysis are characteristically highly reflecting, isotropic chars (no semicokes were observed), which are vesicular and resemble coal gasification chars. More vesicular chars were produced at lower pyrolysis temperatures, suggesting that the products were more gaseous than those obtained at higher temperatures.
3. In spouted-bed pyrolysis, coals of variable type and rank (Onakawana, Forestburg, Sukunka and Fordings) produced variable solid products. Low-ranking Onakawana coal produced significantly large amounts of unaltered coal. For the majority of the coals the amount of unaltered coal decreases as the pyrolysis temperature increases.
4. The dominant component in the spouted-bed pyrolysis residues is altered or reacted huminitic coal; in this way the residues closely resemble the products of more conventional coal liquefaction processes.
5. With the exception of the Forgings coal residues, small amounts (under 4%) of anisotropic semicoke were observed in the solid products from spouted-bed pyrolysis. Semicoke ranged from 16% to 32% of the Fording coal residues. This appears to be controlled by the rank/type of the feed coal.
6. A highly reacted char as well as high-temperature anisotropic coke were included in the spouted-bed pyrolysis residue from the Fording coal. This is also likely to be a function of the coal type/rank.
7. The reflectance of the reacted huminite residues from spouted-bed pyrolysis of Onakawana, Forestburg, Sukunka and Fordings coals is related to the pyrolysis temperature.
8. The solid products from low-temperature/long residence time liquefaction of Estevan lignite are dominantly composed of isotropic, altered coal with variable amounts of anisotropic semicoke. The semicokes were generated at elevated temperatures.

9. The principal product of huminite liquefaction is a granular residue; the amount of granular residue is proportional to the calculated coal conversion. Poorer conversions were obtained when part of the granular residue was anisotropic; this supports earlier observations that restricted liquid yields are caused by semicoke formation.
10. In the solid products from coprocessing of Forestburg subbituminous coal with Cold Lake vacuum bottom oil, much of the residue comes from the oil.
11. The coal/oil coprocessing residues are principally composed of altered coal and a bituminous product, both of which are variably isotropic solids and anisotropic semicokes. The semicokes form mostly in the bituminous solids and are produced under variable reaction conditions, particularly at higher temperatures.
12. Less semicoke is generated in the coal/oil coprocessing residues when the atmospheric gases are H_2S/H_2 mixtures rather than H_2. This is particularly evident in experiments conducted under similar experimental conditions, at relatively high temperatures, i.e., when semicokes are most likely to form.
13. The solid liquefaction products of low-rank coals contain less inertinite than the feedstocks. Unaltered coal in residues generated at lower temperatures comprises mostly inertinite macerals but at higher temperatures much of the inertinite is chemically altered, though not necessarily 'liquefied'.

ACKNOWLEDGEMENTS

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TABLES

Table 1 – Characterization of coal macerals: optical properties in reflected light

Maceral Group	Morphology	Reflectance Colour	Reflectance Intensity
Vitrinites/humanites	structured unstructured groundmass	dark to medium to light gray	intermediate
Inertinites	structured unstructured	light gray to brilliant white	high to very high
Exinites/liptinites	characteristic maceral form	dark brown to gray	weak
Mineral matter	clay minerals pyrite (marcasite) oxides (quartz) (hematite) Carbonates (dolomite) (ankerite) (siderite)	variable	variable

Table 2 – Classification of coal liquefaction residue components

Unaltered coal:	unreacted coal, inertinite, vitrinite/huminite or exinite/liptinite
Altered coal:	isotropic 'vitroplast' (Mitchell et al., 1977) isotropic granular residue (Mitchell et al., 1977) isotropic inertinite anisotropic semicoke (derived from vitrinite/huminite)
Highly altered coal:	isotropic char (R_O >3.0%) anisotropic coke
Pyrolytic carbon	
Bituminous solids:	weakly reflecting, isotropic particles isotropic 'bituplast' anisotropic 'mesophase' spherules anisotropic semicoke
Mineral matter:	crystalline, inorganic minerals present in the feed coal, or derivatives

Table 3 – Petrographic analysis of Forestburg coal

Maceral Group	%
Huminites – structured	61.2
– unstructured	9.2
– groundmass	19.4
Liptinites	3.6
Inertinites	5.4
Mineral Matter	1.2
	100%
Reflectance, % R_o random	0.49

Table 4 – Petrographic analyses of coal pyrolysis chars

Sample number	12 Char 12	13 Char 13	14 Char 14
Unaltered coal	–	–	–
Altered coal			
(i) isotropic:			
– non-vesicular	4.0	3.2	5.6
– vesicular	88.4	83.0	75.6
– highly vesicular	7.0	13.0	18.2
(ii) anisotropic	–	–	–
Mineral matter	0.6	0.8	0.6
	100%	100%	100%
Reflectance, % R_o random	1.46	1.97	2.45

Table 5 – Petrographic analyses of coal feedstocks for spouted-bed pyrolysis

Maceral Group %	Forestburg 1	Forestburg 2	Fordings	Onakawana
Vitrinites/huminites	89.2	90.0	75.2	73.2
Liptinites	3.8	3.2	1.0	3.7
Inertinites	5.6	5.0	22.0	17.2
Mineral matter	1.4	1.8	1.8	4.8
	100%	100%	100%	100%
Reflectance, % R_o random	0.44	0.43	0.89	0.27

Table 6 – Petrographic analyses of spouted-bed pyrolysis residues

	Forestburg				
Sample No.	2	3	4	5	6
% Residue Component					
Unaltered coal	0.8	2.2	.4	0.8	0.0
Altered coal					
– isotropic	96.2	96.0	95.2	95.6	99.4
– anisotropic	3.0	1.0	3.0	3.6	0.2
Highly altered coal					
– isotropic	–	–	–	–	–
– anisotropic	–	–	–	–	–
Mineral matter	0.0	0.8	0.4	0.0	0.4
	100%	100%	100%	100%	100%
% Reflectance R_O random					
– altered coal	2.21	1.64	1.71	2.21	2.73
– highly altered coal	–	–	–	–	–

	Fordings				Onakawana			
Sample No.	1	2	2	4	2A	2B	2C	2E
% Residue component			(agglom)					
Unaltered coal	0.0	0.0	0.0	0.0	15.2	15.2	5.6	3.6
Altered coal								
– isotropic	41.2	23.8	45.2	36.6	81.8	82.4	88.8	91.4
– anisotropic	22.8	32.4	16.4	21.6	1.8	0.8	1.6	1.0
Highly altered coal								
– isotropic	12.6	17.0	11.2	18.6	0.0	0.0	0.0	0.0
– anisotropic	20.4	24.4	15.4	18.8	0.0	0.0	0.0	0.0
Mineral matter	3.0	2.4	11.8	4.0	1.2	1.6	4.0	4.0
	100%	100%	100%	100%	100%	100%	100%	100%
% Reflectance R_O random								
– altered coal	1.31	1.51	1.57	1.51	1.93	2.01	2.11	3.01
– highly altered coal	5.40	5.55	5.09	4.65	–	–	–	–

Table 7 – Petrographic analysis of Estevan lignite

Maceral Group	%
Huminites	
structured	42.6
unstructured	1.8
groundmass	28.4
Liptinites	4.8
Inertinites	19.8
Mineral matter	1.6
	100%
Reflectance, R_O random	0.35

Table 8 – Petrographic analyses of low-temperature liquefaction products of Estevan lignite

Residue % Component	Sample No. 1	4	9	10	18
Unaltered coal	1.2	0.4	4.8	4.8	2.0
Altered coal					
– isotropic	88.0	71.2	91.6	91.2	90.4
– anisotropic	9.2	27.2	2.0	2.0	6.2
Mineral matter	1.6	1.2	1.6	2.0	1.4
	100%	100%	100%	100%	100%
% Reflectance, R_o random	0.99	1.48	1.31	0.85	1.45

Table 9 – Petrographic analysis of Forestburg coal feedstocks for coal/bitumen coprocessing

Sample No. Maceral Group %	Forestburg 1	Forestburg 2
Huminites		
structured	71.8	75.2
unstructured	1.6	2.8
groundmass	18.8	16.0
Liptinites	2.8	2.4
Inertinites	4.2	3.0
Mineral matter	0.8	0.6
	100%	100%
Reflectance, % R_o random	0.42%	0.41%

Table 10 – Relative abundance of coal-derived and bituminous solids in coal/bitumen coprocessing residues

Sample No.	Coal-derived Solids	Bituminous Solids	Mineral
10R	18.8	80.0	1.2
36	13.0	86.2	0.8
37	26.6	69.4	4.0
73	2.3	95.4	2.3
77	1.8	97.0	1.2
78	2.4	93.8	3.8
79	19.0	76.6	4.4
80	18.8	74.1	7.1
82	29.6	70.2	0.2
83	20.4	79.2	0.4
85	9.6	78.4	12.0
86	1.4	88.4	10.2
91	30.0	67.2	2.8
92	3.0	96.0	1.0
105	8.0	90.8	1.2
106	14.4	84.6	1.0
117	0.0	99.6	0.4
118	0.0	99.8	0.2

Table 11 – Percentage isotropic and anisotropic solids in residues from coal/bitumen coprocessing using H_2/H_2S mixtures

Sample No.	Isotropic	Anisotropic	Mineral
10R	90.8	8.0	1.2
36	78.0	21.2	0.8
37	96.6	0.0	4.0
73	90.6	7.1	2.3
77	39.0	59.8	1.2
78	55.2	41.0	3.8
79	95.6	0.0	4.4
80	92.9	0.0	7.1
82	99.4	0.4	0.2
83	99.0	0.6	0.4
85	88.0	0.0	12.2
86	85.4	4.4	10.2
91	93.4	3.8	2.8
92	92.8	6.2	1.0
105	81.0	17.8	1.2
106	84.2	14.8	1.0
117	92.6	7.0	0.4
118	88.2	11.6	0.2

FIGURES

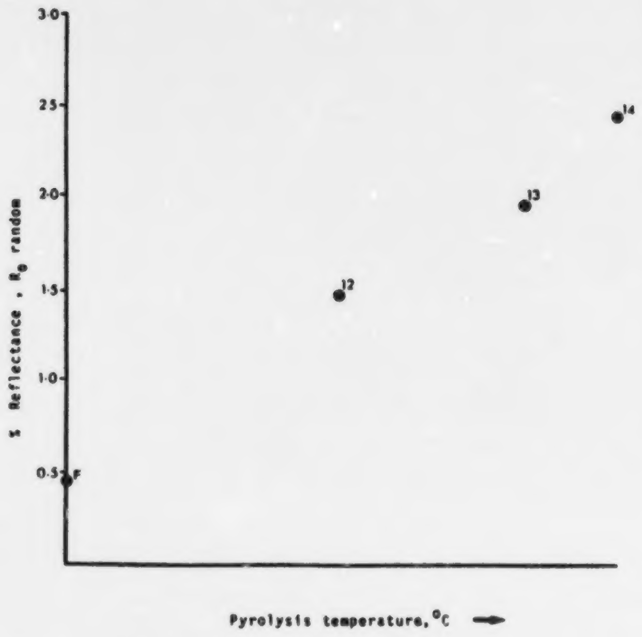

Fig. 1 – Reflectance of chars versus pyrolysis temperature

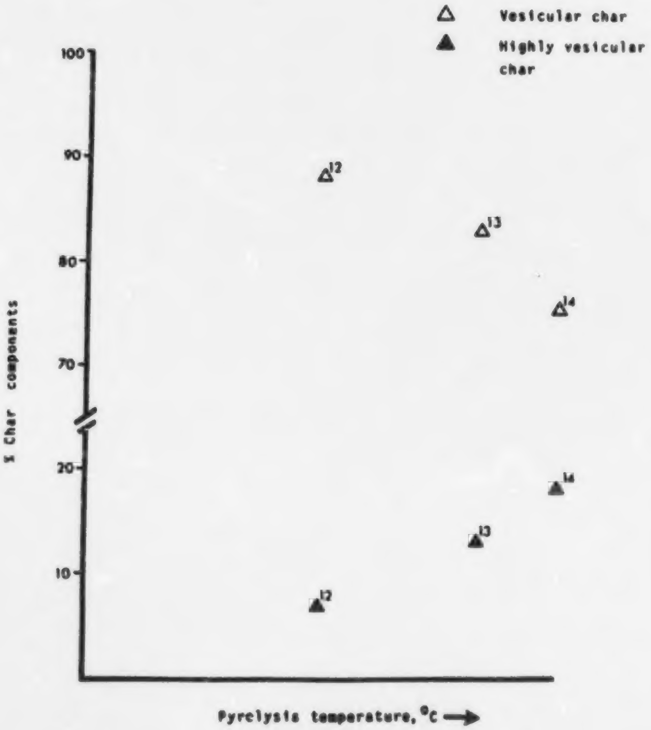

Fig. 2 – Percentage of vesicular and highly vesicular char versus pyrolysis temperature

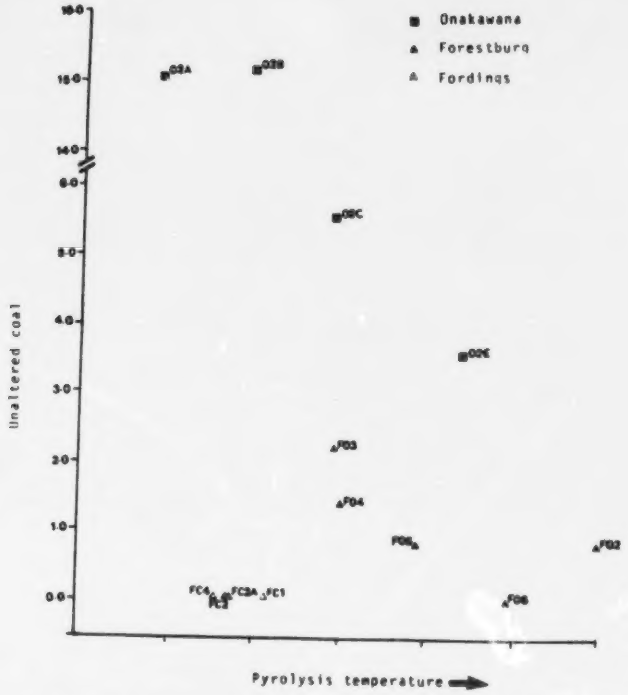

Fig. 3 – Percentage of unaltered coal in the residues versus pyrolysis temperature

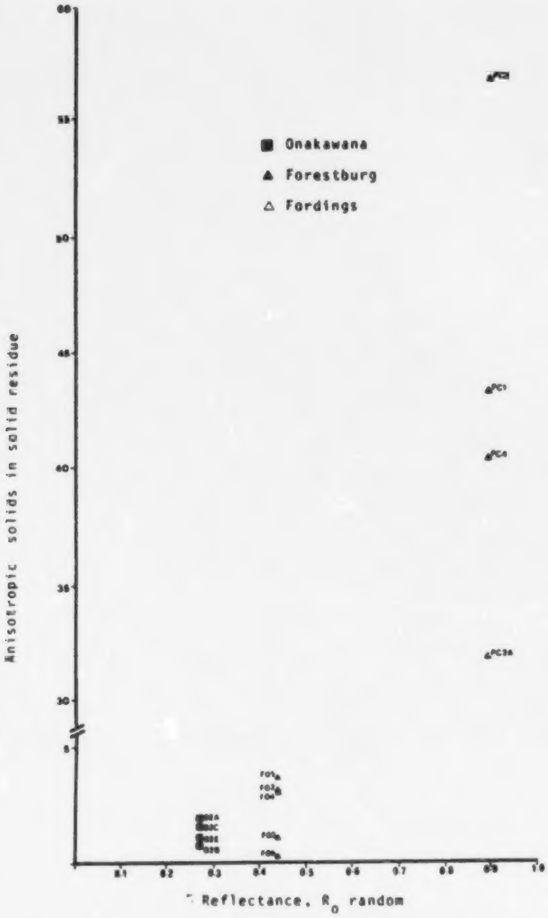

Figure 4 Total anisotropic solids in the solid residue versus vitrinite/huminite reflectance

Fig. 4 – Total anisotropic solids in the solid residue versus vitrinite/huminite reflectance

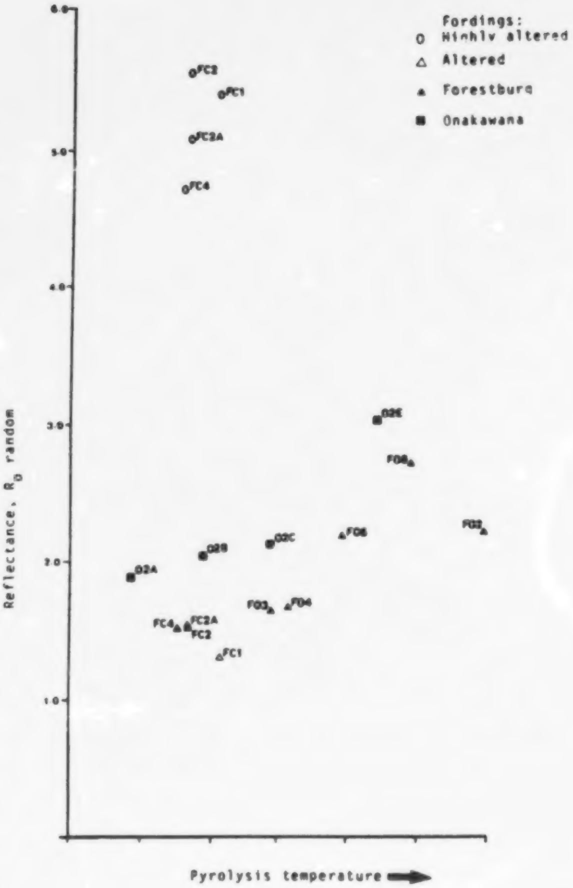

Fig. 5 – Reflectance of the vitrinite/huminite residue versus pyrolysis temperature

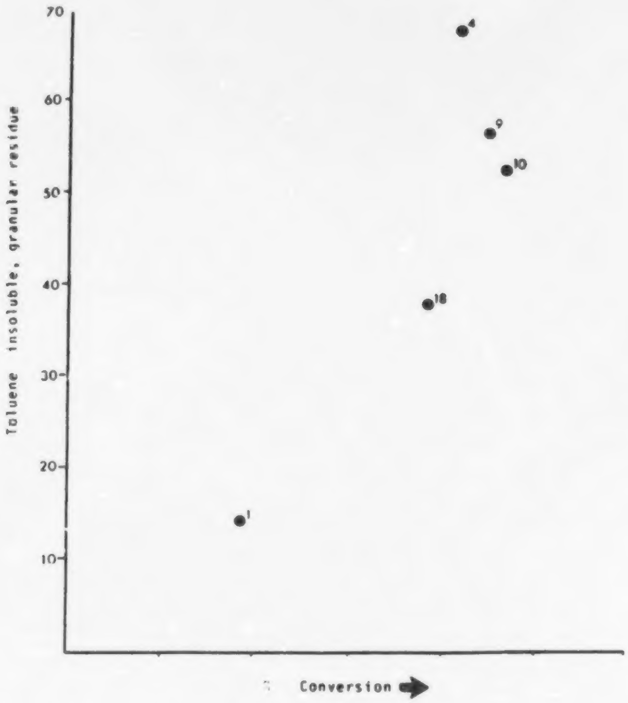

Fig. 6 – Percentage toluene insoluble, granular residue versus conversion

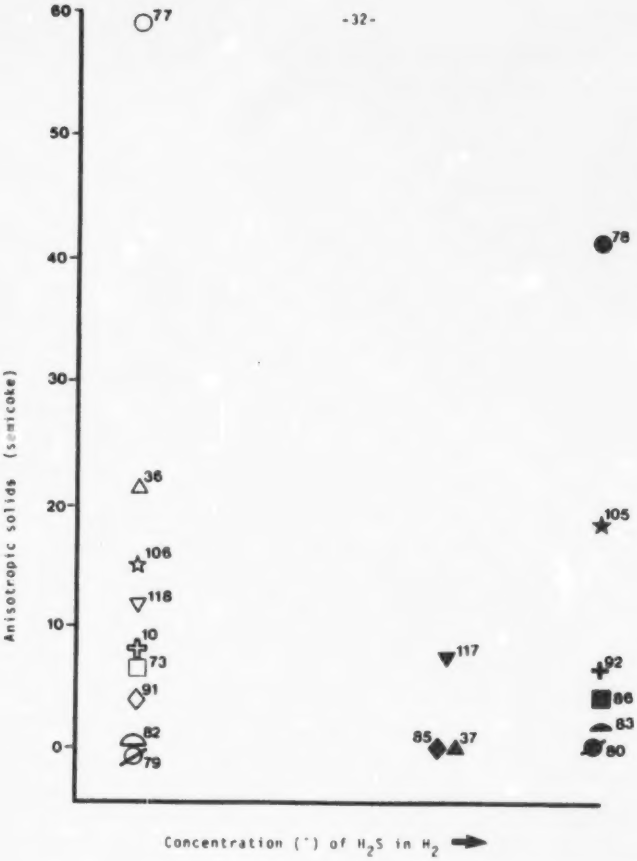

Fig. 7 – Percentage semicoke in the residue from coal/bitumen coprocessing versus % H_2S in H_2

SESSION III: PAPER 14

APPLICATION OF SOLVENT-SALT LIQUID CLATHRATE SYSTEMS TO COAL LIQUEFACTION

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ABSTRACT

Certain main group and potentially catalytic transition metal salts dissolve in aromatic solvents (toluene, xylene) to form highly ionic polar liquid clathrate phases that have the novel property of coexisting with the pure solvent phase.

Such liquid clathrate systems have the capability for dissolving significant coal solid and heavy bitumen under low-temperature conditions with the added advantage of continually stripping the oil and asphaltene fractions into the coexisting collector phase.

A range of western Canadian and representative eastern coals have been studied for solubilization in liquid clathrates derived from a range of salts; they include hexamethyl disilazides and $M^+[Al_2(C_2H_5)_6X]^-$ where $X = Cl^-, I^-$; and the counter ion M^+ ranges from quaternary ammonium to transition metal ion, e.g., $[Fe(C_5H_5)(arene)]^+$.

The extraction efficiency is highly rank-dependent for the western coals, reaching a maximum at ca 85% carbon as predicted for a purely physical process. In agreement, yields are dependent on contact time, the nature of the salt and coal subdivision; approaching or exceeding the efficiency of the interactive coal-specific solvent pyridine (15-25% daf for medium- to high-volatile A bituminous coal). Mass balances of 95 to 100% are consistent with physical dissolution.

Catalysts based on transition metal salts with known capacity for reducing aromatic structures have been incorporated directly into the clathrate phase both as co-dissolved salts and as an integral element of the ionic clathrating system. In situ upgrading studies employing these solvent-bound catalysts during clathration at low hydrogen pressure are discussed.

The mild conditions of the physical dissolution have facilitated examination of the asphaltene (aromatic soluble) and preasphaltene (clathrate/pyridine soluble) phases from a coal structure standpoint employing g.c., g.c./m.s., and gpc separations, vapour phase osmometry, and a range of spectroscopic techniques. Aromaticity evaluation by ^{13}C and ^{1}H n.m.r. using $AsCl_3$ (arsenic trichloride) as a solvent has been particularly effective.

**denotes speaker*

PRÉSENTATION 14

APPLICATION À LA LIQUÉFACTION DU CHARBON DES SYSTÈMES À CLATHRATE LIQUIDE SOLVANT-SEL

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RÉSUMÉ

Certains grands groupes de sels de métal de transition, possiblement catalytiques, se dissolvent dans des solvants aromatiques (toluène, xylène) pour former des phases de clathrate liquide polaires très ioniques ayant la propriété originale de coexister avec la phase de solvant pur.

Ces systèmes de clathrate liquide peuvent dissoudre beaucoup de solides de charbon et de bitume lourd, même à faible température, tout en offrant l'avantage supplémentaire de décaper sans arrêt les fractions d'asphaltène et de pétrole jusqu'à l'étape de collection coexistante.

Une gamme de charbons de l'Ouest canadien et de charbons représentatifs de l'Est ont été étudiés en vue de la dissolution en clathrates liquides, à partir d'un éventail de sels, notamment les disilazides hexaméthyl et $M^+[Al_2(C_2H_5)_6X]^-$ lorsque $X = Cl^-, I^-$, et le contre-ion M^+ varie de l'ammonium quaternaire à l'ion métallique de transition, e.g., $[Fe(C_5H_5)\ (arene)]^+$.

L'efficacité d'extraction dépend beaucoup du rang, dans le cas des charbons de l'Ouest, et atteint un plafond de ca 85% de carbone, comme prévu, dans le cas d'un procédé purement physique. En accord, les rendements dépendent du temps de contact, de la nature du sel et de la subdivision du charbon, et approchent ou dépassent le rendement du solvant de pyridine interactif spécifique au charbon (15 à 25 % daf dans le cas du charbon bitumineux A très volatil). Les équilibres massiques de 95 à 100 % sont consistants avec la dissolution physique.

Les catalyseurs basés sur des sels métalliques de transition ont été intégrés directement à la phase clathrate. Les études de valorisation in situ, utilisant ces catalyseurs liés par solvant, durant la clathration à de faibles pressions d'hydrogène, sont décrites.

Les conditions douces retenues ont facilité l'examen de la matière produite par la phase de clathrate pré-asphaltène, dans une perspective d'examen de la structure de charbon. L'évaluation de l'aromaticité par ^{13}C et ^{1}H NMR, en utilisant de l'$AsCl_3°$ (trich1orure d'arsenic) comme solvant, s'est avérée fort efficace.

**indique le conférencier*

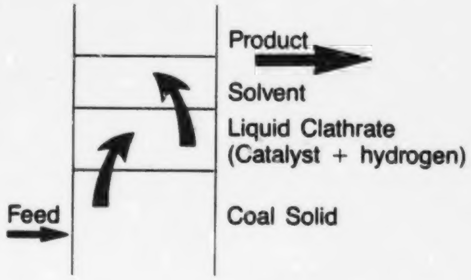
APPLICATION OF SOLVENT-SALT LIQUID CLATHRATE SYSTEMS TO COAL LIQUEFACTION

THE LIQUID CLATHRATE CONCEPT

The basic premise for exploring novel technologies for coal conversion lies in the growing consensus that adverse thermodynamic (energetic) and technological considerations are present in high-temperature coal hydroliquefaction, extraction and gasification processes. Alternative approaches, including coprocessing options, attempt to reduce the severity of the operating conditions in some measure by increasing the mobilization of the coal mass, either through solvation or more effective catalysis.

In the present study it has been argued that a combination of the enhanced dissolving power of aromatic solvent-salt phases, known as liquid clathrates, could be used to achieve such mobilization of the coal solid at lower temperatures. Moreover, since such phases can coexist with a solvent phase, it would be possible to strip product from the clathrate phase with a collector solvent.

Conceptually, the approach is illustrated by the diagram below:



It is implicit in the model that only physical dissolution (or dispersion of the coal mass in the highly ionic clathrate phase) occurs initially.

Subsequently, a catalyst or chemical agent present as a dissolved salt or integral element of the clathrating medium must effect useful upgrading of the macromolecules under moderate conditions of temperature and hydrogen overpressure as indicated in the diagram.

The *liquid clathrate* solvent systems were discovered by Professor J.L. Atwood at the University of Alabama.

As part of a general study of compounds related to so-called Ziegler-Natta catalysis, Ziegler and co-workers reported in 1960 the synthesis of compounds of the type $M[Al_2R_6X]$ according to Equation 1.

$$2AlR_3 + MX \rightarrow M[Al_2R_6X] \qquad \text{Eq 1}$$

On attempting to dissolve $K[Al_2Me_6N_3]$ in benzene, Atwood found the material dissolved quickly, and two liquid layers were observed. Subsequently, the scope of Equation 1 was rapidly expanded and the liquid-layering effect was obtained for virtually all combinations of M, X, and R, e.g., Table 1.

By n.m.r. spectroscopy, it has been established that the lower clathrate phase for $K[Al_2Me_6]N_3$ has 5.8 benzene molecules per ion pair.

While the original term clathrate had been restricted to solids, the novel properties of the ionic phases led Atwood to coin the phrase *liquid clathrates*. Some of the most important properties are as follows:

1. The behaviour is observed *only* in aromatic solvents.
2. All of the parent compound is confined to the lower layer. The upper one contains only the excess aromatic.
3. For a given set of M, X, R, and aromatic the lower layer will only load a given constant amount of aromatic, referred to as the A/A (aromatic-to-anion) ratio.
4. The aromatic is trapped by, not bonded to, the parent compound and may be freed in some cases by a small change in temperature.

The phenomenon is not restricted to the complex aluminates but has been observed for silazides of the structure $NA^+[NSi(Me)_3]^-_2$, provided the sodium ion is complexed by a crown ether.

A more extensive introduction to the background of these novel liquid-liquid phases has been provided in the proceedings of the previous coal contractors' meeting (1), and in the literature (2).

In our current program, liquid clathrates based on triethylaluminum and a range of complexing salts (mainly tetra-n-propyl ammonium iodide) have been used, principally in toluene or mixed xylenes as solvent. In laboratory quantities, the clathrates are readily prepared as follows:

> *Material routinely used for coal extractions was made in about 500-ml batches. One hundred g of NPr_4I (0.319 mole) was placed in a 1000-ml Erlenmeyer flask and transferred to the inert atmosphere glove box. Five hundred ml of distilled toluene (stored over molecular sieves) was poured over the salt and 87 ml (0.638 mole) of $AlEt_3$ was slowly added. Following mixing for 5 minutes approximately 500 ml of liquid clathrate formed and all the NPr_4I dissolved. The Erlenmeyer was stoppered and the liquid clathrate stored in the inert atmosphere glove box until needed. The liquid clathrate was stable indefinitely under these conditions.*

MOBILIZATION OF THE COAL SOLID

Interest in the use of liquid clathrate extraction was sparked by Atwood's observation that on contact with <100 mesh Mary Lee Seam Alabama coal, the clathrate phase immediately darkens, and transfer to supernatant toluene is evident.

Atwood reported that approximately 20% of the coal solid was mobilized in the clathrate phase on exposure to the clathrate at a ratio of 10 ml of liquid phase to 1 g of coal that had been dried by heating at 110°C for 24 hours. The azide salts employed in these studies lend themselves to separation from the clathrate phase by fractional crystallization. Subsequently, yields were determined by distillation of the organic material in the solvent and clathrate phases.

For evident reasons of safety in more intensive characterization of the resulting heavy oil fractions, we have chosen to use other salts and a low-temperature hydrolytic workup to preserve the structural features of the products. In practical terms considerable exploratory study was undertaken in establishing the approach shown in Scheme 1.

The result can be summarized simply: the toluene phase provides both *oil* (pentane or hexane soluble) and *asphaltene* (toluene soluble) material, while the cold pyridine extraction of the residue and clathrate mobilized material has been equated with the preasphaltene fraction defined for high-temperature liquids.

Several comments are appropriate. First, for extraction of the product from heavy (salt) media like the clathrate phase, centrifugation is essential to collect the coal fines fraction in the solid residue. These steps were taken by transferring the slurry to centrifuge tubes under nitrogen, and employing septrum caps in the subsequent centrifugation. Secondly, in our hands complete removal of entrained pyridine was only possible employing the 10% HC1 precipitation technique. Only under these conditions with extensive water washing was it possible to remove both pyridine and pyridine hydrochloride from the resulting product (preasphaltene) as judged by n.m.r. spectroscopy.

COMPARATIVE STUDIES

In order to characterize the process occurring with clathrate dissolution, we turned to the other available low-severity physical process – solubility in classical solvents. The yields for the obvious options – refluxing toluene b.p. 110°C and refluxing pyridine b.p. 118°C – are shown in Table 2 for a series of coals of differing rank. Special emphasis in the clathrate experiments has been placed on two of these coals: *K-seam*, a medium-volatile A bituminous Cretaceous coal from Fording Coal in British Columbia, and Devco, a Nova Scotian coal with the higher sulphur characteristic of these eastern (Carboniferous) coals. Analytical data for a range of coals used in the study is shown in Table 3a. Maceral analysis was obtained for a number of target and B.C. coals; while variations are evident, the K-seam and Devco bituminous coals are *comparable* in vitrinite, but the internite/semifusinite content of the K-seam (Cretaceous coal) is somewhat higher as is always found (Table 3b).

In Table 4 the pyridine soluble material has been broken down into a toluene soluble fraction and residual pyridine soluble material. The data was obtained by simple sonication in toluene of the raw pyridine soluble product obtained by precipitation with HC1 in the same manner as the clathrate phase workup (Scheme 1). Note the rather *higher* yield of toluene soluble material by this indirect route than by direct reflux with toluene, a phenomenon likely related to physical swelling of the coal by pyridine freeing additional asphaltene material from the solid matrix. Incidentally, the solubilities are rather lower than some literature reports. For example, a pyridine reflux solubility of Illinois 6 as high as 23% has recently been reported (3), though in our hands only 12% was obtained by reflux and precipitation. We find extensive washing with dilute HC1 is necessary to remove residual solvent, even employing precipitation for these reflux experiments as well. Moreover, the yields reported are those for simple filtration (Whatman 40 paper) and would be doubtless further reduced by either micropore filtration or ultracentrifugation (4).

The clathrate extraction data in Table 4 for the two coals differs slightly from the pyridine reflux results in that a further subdivision of the preasphaltene material by chloroform extraction has been made. However, several features are evident: (i) the toluene solubility, i.e., without clathrating salt is predictably extremely low; (ii) the overall net yields (both extractions ca., 120°C) for clathrate and solvent are similar; (iii) in favourable cases (Devco) a substantial fraction >20% of the coal is mobilized.

A tentative hypothesis is immediately presented:

1. The liquid clathrate phase is functioning as a solvent in a strictly physical sense.
2. Its efficiency for the two coals does not differ from the classical near-optimum solvent pyridine.

Two further questions are suggested:

1. Is the rank dependence of the process the same in the two instances?
2. Are there any significant differences (molecular weight, aromaticity or functional groups) in the nature of the material that is extracted by the two media?

VARIATION WITH RANK

Classical solvents usually exhibit a maximum dissolution of the coal solid near 85%C daf. Examination of Figure 1 shows that in our hands the rank dependence of the clathrate media does not differ significantly from pyridine. Accordingly, both coals of low-rank such as Forestburg and a Canmore anthracite provide small-to-negligible yields of soluble material on prolonged extraction.

CHARACTERIZATION OF SOLVENT-CLASS FRACTION

Since the direct extraction yields for clathrate and pyridine are evidently analogous for K-seam and Devco, further examination of solvent fractions was undertaken to compare their physical analytical and spectroscopic properties.

As the following data will emphasize, it is clear that at least for these two bituminous coals that are effectively dissolved by these two polar solvent media, any qualitative differences in elemental composition, structure or molecular size are minor compared to the striking similarities that are observed.

Nuclear Magnetic Resonance Spectroscopy

Both ^{13}C and ^{1}H spectroscopies were applied to the solvent fractions obtained from the clathration experiments, and from reflux solvent extractions. For the nonpolar toluene (and chloroform) soluble material, conventional $CDCl_3$ solutions were used. For the *toluene* soluble material (oil plus asphaltene) the comparison between coals is affected by changing aromatic-to-aliphatic ratio with time of extraction, a phenomenon previously reported in n.m.r. studies of solvent fractions. Figure 2 shows the variation in Har/Hal for extended extraction of a K-seam coal with a tetra-n-propylclathrate in toluene. Notwithstanding, the *final* Har/Hal ratio for the toluene soluble material from the Devco and K-seam coals shows no variation within the experimental error based on measurements to date.

Material of preasphaltene type is more representative of the clathrate extraction process (Table 4) and can be compared with the other high-yield solvent pyridine. In the case of this less tractable preasphaltene we faced the usual problems of partial dissolution (CS_2) or interference from residual proton content (i.e., d-5pyridine). We resorted to a solvent previously used in the polymer field, $AsCl_3$ (5).

In using this material, it is *mandatory* to perform all transfers in the fumehood, and to wear protective glasses. *The hazardous nature of the material should be recognized*. Sample tubes are sealed (paraffin or polythene film) to protect against absorption of moisture by hygroscopic $AsCl_3$. Samples prepared in this fashion show no deterioration (spectral changes) over 48 hours, though spectra are normally recorded immediately. Figure 3 shows a preasphaltene fraction proton spectrum for K-seam employing this solvent system. For ^{13}C spectra, we employed 350 mg of preasphaltene in 3 g of solution. Qualitatively, ^{13}Cmr spectra in $AsCl_3$ were recorded, though for quantitation, 0.005 M $Cr(AcAc)_3$ was added. Dissolution in all cases was ensured by sonication in a water bath for 10 minutes.

Both simple comparison of the fraction of the carbon atoms and of the protons that are aromatic (f_a^* and F_a^* values, Table 5) and extended subdivision of the aliphatic hydrogen envelope (6) (Appendix, Table 1) were carried out. As Table

5 shows, the variation in our hands from run to run encompasses the differences in the observed ratios. We are persuaded that for these coals of similar rank, no systematic trends are apparent between the two techniques, or *between* the two coals.

Elemental Analysis of Coal Fractions

Close correspondence between the f_a^* and F_a^* values for *clathrate* and *pyridine* extracts prompted elemental analysis (carbon and hydrogen) of a series of preasphaltene fractions, shown in Table 6. For continuity in the present comparison, only data from Devco and K-seam coals are shown. One can see that differences between the clathration and refluxing pyridine systems are close to the expectations for the complexity of the work-up procedures. In particular, for the Devco coal the soluble material *with* asphaltene and oil removed is similar in composition for the two approaches. Coal residues are lower in hydrogen content, but far from depleted. Nitrogen values are disturbingly high relative to current analyses of the coals (particularly K_B). Standard analysed samples of Illinois #6 from the Illinois State Geological Survey have been received and are being used, as in analytical control tests, to see if pyridine incorporation is occurring.

Macromolecular Components: Vapour phase osmometry and thermal gravimetric analysis (TGA)

Since the overall properties of the pyridine soluble fractions clearly allow little discrimination by n.m.r. or elemental analysis, further subdivision of the material is being undertaken currently.

The approach adopted has been to partition the material on a thermostatted LH20 Sephadex column in dry pyridine, recover the material by precipitation in large volumes of 10% HC1, and measure the molecular weight by vapour phase osmometry in dry pyridine relative to benzil and carbowax (MW 1000) standards.

As Table 7 shows, for Devco and K-seam the results using this approach show relatively poor discrimination on LH20, and a tendency for random failure of the molecular weight measurement (fraction 1, Devco). The latter problem may be associated with the extreme sensitivity of these fractions to manipulation (i.e., precipitation and redissolution). Accordingly, recently we have begun to measure molecular weight directly on an aliquot from each fraction and back calculate the concentration from the recovery of solid from the remainder of the fraction. As Table 7 shows, this appears to be a superior procedure, and further measurements are in progress.

Thermal gravimetric analysis (TGA) offers a means of *comparing* materials whose low volatility may make them unsuitable for gas chromatographic study. In collaboration with B.C. Research, Vancouver, B.C., we have obtained TGA profiles employing their instrumentation for the toluene soluble material in the clathrate extraction of Devco and K-seam coals, Figures 4(a) and (b). The striking similarity of temperature dependence in slope and weight per cent suggests to us again that the inherent macromolecular distribution in these two coals may be extremely similar, reflecting the greater influence of coalifaction (rank) than other geologic parameters.

Examination of the TGAs from the preasphaltene (clathrate soluble) material from the K-seam and Devco clathration experiments again shows that volatility is comparable, though now much less volatilization occurs prior to the 525°C temperature cut off. A typical thermogram for Devco clathrate soluble material is shown in Figure 5. Note the low ash content (arrow).

Volatile Components: Comparison by Gas Chromatography-Mass Spectrometry (gc/ms)

While gc volatile material is a small fraction of the net weight from the extractions, it is a valuable indicator of the differences in coalification (and geology) of the substrates. In this work, we have separated an *oil* fraction from the toluene soluble material derived from *both* pyridine reflux and clathration for K-seam and Devco coals. Additionally, we have obtained oil fractions from toluene reflux extracts for both coals.

Experimentally, a pentane fraction was obtained by exhaustive washing of the initial toluene soluble material through a Silica *Sep-pak*. Approximately 75±5% of the material was eluted, and subsequently examined by capillary gc/ms using both C.I. and E.I. detection. While detailed examination of all the data is beyond the scope of this report, it is instructive to examine the C.I. chromatograms [Fig. 5(a) and (b)] and the associated assignment of peaks based on retention indicies (Appendix, Table 2) for a toluene fraction from pyridine reflux (isolated by sonication) and a toluene fraction from 120°C clathration (mixed xylenes) both based on Devco coal. Note that a series of standards (naphthalene, phenanthrene, anthracene and chrysene) have been added.

Clearly, *no* significant differences in the components in the toluene phases from two samples are revealed. This data suggests that the predominantly physical nature of the clathration phenomenon is well established, and that the measurement of catalytic activity in the clathrate phase can be made both by gcms and gravimetric study of the stripping solvent.

CATALYTIC UPGRADING IN CLATHRATE MEDIUM

Introduction

It is clear from the foregoing discussion that the clathrate/solvent medium is capable of mobilizing coal with approximately the same efficiency as pyridine (i.e., ca 23% dissolution, compared with 4% in benzene, 0.1% in cyclohexane under comparable conditions), although the material extracted may not be the same in each case. The action of the clathrate phase upon the coal is a physical process whose nature is not yet understood and remains a complex problem which is inextricably bound to the yet indeterminate general structure of coal. The advantage of the clathrate treatment over pyridine extraction lies not in the area of % dissolved yield, however, but in the potential of the clathrate for supporting and retaining an upgrading catalyst which will effect hydrogenation under mild conditions of temperature and pressure. Identification of a suitable clathrate-soluble hydrogenation catalyst would open up the possibility of upgrading clathrate-soluble coal-derived material with consequent phase-transfer from clathrate into the solvent phase. It should be noted that a homogeneous catalyst will be required for this application: conventional heterogeneous upgrading catalysts are not designed to work at low-temperatures and would be susceptible to physical poisoning under the conditions employed. Since little information is available concerning solvation or solvolysis effects in the clathrate phase, identification of a solute which will act as a homogeneous hydrogenation catalyst in such an unusual chemical environment is a serious problem. Accordingly, as a starting point we have concentrated our attention around the previous claims of the Alabama group. We have also recently begun to examine the stability of several established molecular transition-metal catalysts in the clathrate in relation to effectiveness for hydrogenation of model unsaturated organics.

Choice of Catalyst

Identification of a hydrogenation catalyst compatible with the clathrate medium and suitable for in situ upgrading of solubilized coal-derived material is subject to several severe constraints including the following:

a. Catalyst activity must be maintained at temperatures not exceeding 120°C and activity at ambient would be an advantage. The catalyst must ideally also be effective at low hydrogen pressures.

b. The catalyst must be soluble in, and be unaffected by, the clathrate or be alkylated by it to a species possessing comparable (or superior) activity. The active species must be stable over long periods in the clathrate phase.

c. Ideally, the catalyst should be immobile in the clathrate phase, i.e., transfer to the solvent phase should be prevented by solubility characteristics of the active species.

These considerations immediately rule out a range of well-established homogeneous transition-metal catalysts so that our approach has been to assess the early reports from the Alabama group while at the same time setting up a systematic examination of the problem.

Transition-metal Additives

It has been suggested on the basis of experiments conducted at the University of Alabama that certain organometallic complexes enhance coal-extraction by liquid clathrates (7). We have tested the effect of the following compounds upon yields of soluble material obtained from Devco and K-seam coals: $(\eta^5\text{-}C_5H_5)Mn(CO_3)$, $(\eta^5\text{-}MeC_5H_4)Mn(CO)_3$, $(Fe(\eta^5\text{-}C_5H_5)_2$, $(\eta^6\text{-mestiylene})Cr(CO)_3$.

In all cases runs were conducted at 70°C for 4hr under 1 atm of H_2, with 2 g additive, 10 g coal, and 100 ml each of liquid clathrate and toluene. No measurable effect upon yield or composition of soluble coal-derived material was observed for any of these additives, although contamination of the toluene phase above the liquid clathrate with transition-metal complex or derived material made exact yield-determinations difficult.

It has been found that transition-metal cations of the type $[Fe(\eta^5\text{-}C_5H_5)(\text{arene})]^+$ and $[Mn(CO)_3(\eta^6\text{-arene})]^+$ are able to sustain liquid clathrate behaviour (as their PF_6^- salts, with $AlEt_3$/toluene). These transition-metal containing liquid clathrates are stable for months under ambient conditions, although in a minor side-reaction alkylated, neutral metal compounds form slowly under typical extraction conditions. It has subsequently been shown, however, that incorporation of these novel liquid clathrates (aromatic = tetralin, mesitylene) in extraction experiments conducted under ambient pressure of hydrogen gas results in no increase in coal liquid yield, although quantification was once again complicated because of the presence of additive-derived materials in the solvent phase. On the basis of these experiments we are of the opinion that some of the conclusions arrived at by the Alabama group may be in error.

The cobalt complex $Co[P(OMe)_3]_3(\eta^3\text{-}C_3H_5)$, 1, was first reported by Muetterties and coworkers (8) and has subsequently been shown to hydrogenate arenes and polycyclic aromatics at room temperature in non-polar solvents (9). Although one report has suggested that 1 is not suitable for coal liquefaction (10), this was under experimental conditions that do not resemble those operating in a liquid clathrate extraction. For this reason 1 was chosen as a possible candidate for clathrate compatibility; however, it was found to decompose rapidly on contact with liquid clathrate to give a reaction mixture which was not active in hydrogenation.

The ruthenium (II) complex $RuCl_2[P(C_6H_5)_3]_3$, 2, and its hydrido-derivatives are well established as catalysts in a number of roles, including reactions hydrogenation of alkenes and hydrogen-transfer reactions (11). It has been demonstrated previously that 2 remains active in the presence of Lewis acids including $AlMe_3$ (12), so that decomposition was not anticipated in the liquid clathrate medium. We have so far been able to demonstrate that 2 remains active for alkene hydrogenation in the clathrate phase: Table 8 lists some results, using 1-octene as a model substrate, which show that efficiency as a hydrogenation catalyst is not markedly affected by the presence of liquid clathrate. The only obvious difference between clathrate and non-clathrate reactions is that isomerization as well as hydrogenation is observed in the presence of liquid clathrate, an interesting observation which suggests a useful modification to the catalyst performance.

A more complete evaluation of 2 is now in progress. We have also begun a parallel investigation using *Wilkinsons' catalyst*, $RhCl[P(C_6H_5)_3]_3$, 3. An earlier study has indicated that homogeneous rhodium catalysts are catalytically active in relation to hydrogenation of coal-derived liquids under mild conditions (13). Since 3 is known to be more effective than 2 towards arene hydrogenation, it may prove to be a useful model in the context of clathrate-mediated upgrading. It is to be expected that these systematic studies will allow us to determine whether immobilization of a soluble cationic transition-metal catalyst in the clathrate phase is a practical proposition. Should this prove to be the case possible applications extend far beyond the upgrading of coal-derived liquids.

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TABLES

Table 1 – Components of the $M[Al_2R_6X]$ parent compound

M	R	X	
Na^+	$-CH_3$	F^-	$HCOO^-$
K^+	$-C_2H_5$	Cl^-	NO_2^-
Rb^+	$-C_3H_7$	Br^-	O_2^-
Cs^+	$-C_4H_9$	I^-	OH^-
NR_4^+		N_3^-	SO_4^{2-}
PR_4^+		SCN^-	CO_3^{2-}
$(C_6H_6)_2Cr^+$		$SeCN^-$	O^{2-}
$(C_5H_5)_2Co^+$		No_3^-	
Ba^{2+}		CH_3COO^-	

Table 2 – Solvent reflux yields vs $\overline{R}_o$

Coal	Toluene Reflux %	Pyridine Reflux %	% Ash	Corrected Reflux %	$\overline{R}_o$	Clathrate % (daf)
Forestburg	0.18	2.97	—	~3	<0.4	NEG
Merritt	0.57	4.32	21.2	5.5	0.82	—
K-seam	0.85	13.7	3.4	14.2	0.90	15.0
Devco	0.26	20.5	~7.0	21.7	0.92	21.0
Mary Lee	0.17	21.4	13.6	24.8	0.94	24.0
Balmer Low[2]	—	6.3	9.0	6.9	1.17	9.6
Balmer High[2]	—	2.6	9.3	2.9	1.33	7.7
Canmore	negligible		—	—	>3.00	NEG

[1] *Clathrate yields are in the combined percentage for all solvent fractions, compared at 118°C (temperature of refluxing pyridine) for 18-hour extraction. Correction for ash content has been made*

[2] *The Balmer samples differ in the $\overline{R}_o$ values*

Table 3(a) – Analytical data of coal samples (%)

Coal	C	H	N	S	Ash	Moisture
Hat Creek	45	2.8	0.7	0.39	26.6	23.5
Illinois #6	66.77	4.65	1.49	0.68	5.91	1.43
Quinsam	71.49	4.48	0.92	0.39	11.33	4.01
Devco	73.24	4.65	1.57	1.69	6.83	2.86
K-Seam	81.38	5.04	0.8	0.75	3.45	1.50
Forestburg	58.63	3.71	1.26	0.50	7.48	10.0
Quinsam	69.23	4.75	0.88	0.38	10.15	3.66
Mary Lee	68.82	4.63	—	—	13.67	0.82
Canmore	86.64	3.62	—	—	—	—
Merritt	63.70	4.51	—	—	21.2	1.67

Table 3(b) – Maceral analysis

	Vitrinite		Liptinite		Inertinite		Semi-fusinite		M.M.		Total Counts
		%		%		%		%		%	
Devco	331	66.2	95	19.0	31	6.2	10	2.0	33	6.6	500
Granby	127	25.4	42	8.4	8	1.6	1	0.2	322	64.4	500
Mary Lee	331	66.2	53	10.6	29	5.8	—	—	87	17.4	500
Quinsam	339	67.8	71	14.2	47	9.4	21	4.2	22	4.4	500
Telkwa	289	57.8	112	22.4	—	—	7	1.4	92	18.4	500
Merritt	226	53.2	127	25.4	1	0.2	7	1.4	99	19.8	500
K-seam	327	65.4	55	11.0	65	13.0	42	8.4	11	2.2	500

Table 4 – Solubility (solvent class) breakdown for pyridine reflux and liquid clathration of K-seam and Devco coals.

		Toluene Soluble	Chloroform Soluble	Pyridine Soluble[2]	Total daf
Devco[1]	A. Clathration	1.9	4.1	15.0	21.0
	B. Pyridine Reflux	3.0	—	17.2[3]	21.7
K-seam	A. Clathration	1.6	2.6	10.8	15.0
	B. Pyridine Reflux	2.7	—	7.0	9.7[4]

[1] *Overall recoveries approach 93%. 10% HCl dissolves 7 weight per cent of Devco coal on reflux, potentially carbonate mineral matter*

[2] *Cold pyridine extraction. For Devco coal, the coal residue yields only 2% of these pyridine solubles*

[3] *Sonication in chloroform dissolves 9.6% of the pyridine soluble material*

[4] *An unusually low value (under study). Previous reflux yields were in 14% range*

Table 5 – ^{1}H and ^{13}C NMR data

Reaction No.		Treatment	f_a^*	$F_a^{\neq}$
K-seam	11-2-9	pyridine reflux	.72	.36
K-seam	11-2-11	pyridine reflux	.77	.42
K-seam	2-47-B	clathration	.69	.36
Devco	11-10-9	pyridine reflux	.74	.30
Devco	10-29-C	clathration	.71	.29
Mary Lee	11-14-2	reflux	.76	.40

* *Fraction of carbon atoms which are aromatic*

≠ *Fraction of protons which are aromatic*

Table 6 – Elemental analysis

	Carbon %	Hydrogen %	Nitrogen
Devco Clathrate (10-38)			
Pyridine Soluble	80.19	5.31	2.62
Coal Residue	76.43	5.20	1.77
Devco Pyridine Reflux (11-10-9)			
Pyridine Soluble	82.97	5.97	1.88
Pyridine Soluble Less Toluene Soluble*	81.69	5.27	—
Coal Residue	77.52	4.92	2.11
Devco (Coal)	73.24	4.65	1.57
K-seam			
Soluble Clathrate	78.36	5.75	2.07
Reflux*	81.13	5.41	1.81
Residue Clathrate	77.83	4.92	1.77
Reflux	77.73	4.78	1.76
K_B (Coal)	80.90	5.05	0.80

Contains chloroform soluble material. In the case of Devco coals we have analysed the toluene-soluble material from the clathrate workup C: 85.20 H: 7.59, indicating the expected higher values

Table 7 – Subdivision of pyridine soluble fractions from clathrate

	K-seam (2-53C) (Precipitation)			Devco (10-12) (Precipitation)			Devco (10-64) (Aliquot)	
	Weight %[1]	M.W.[2]		Weight %[3]	M.W.		Weight %[4]	M.W.
V_1	33.5	1338	V_1	26.0	(269)	V_1	11.0	4463
V_2	26.7	1328	V_2	34.3	1453	V_2	21.4	4365
V_3	12.2	662	V_3	10.2	1173	V_3	24.6	4566
V_4	5.4	465	V_4	5.3	*	V_4	16.4	2943
V_5	1.6	*	V_5	3.9	*	V_5	9.0	1933

[1] *30 ml fractions*
[2] *Measured in pyridine employing benzil and carbowax standards*
[3] *15 ml fractions*
[4] *10 ml fractions*
* *no measurements made*

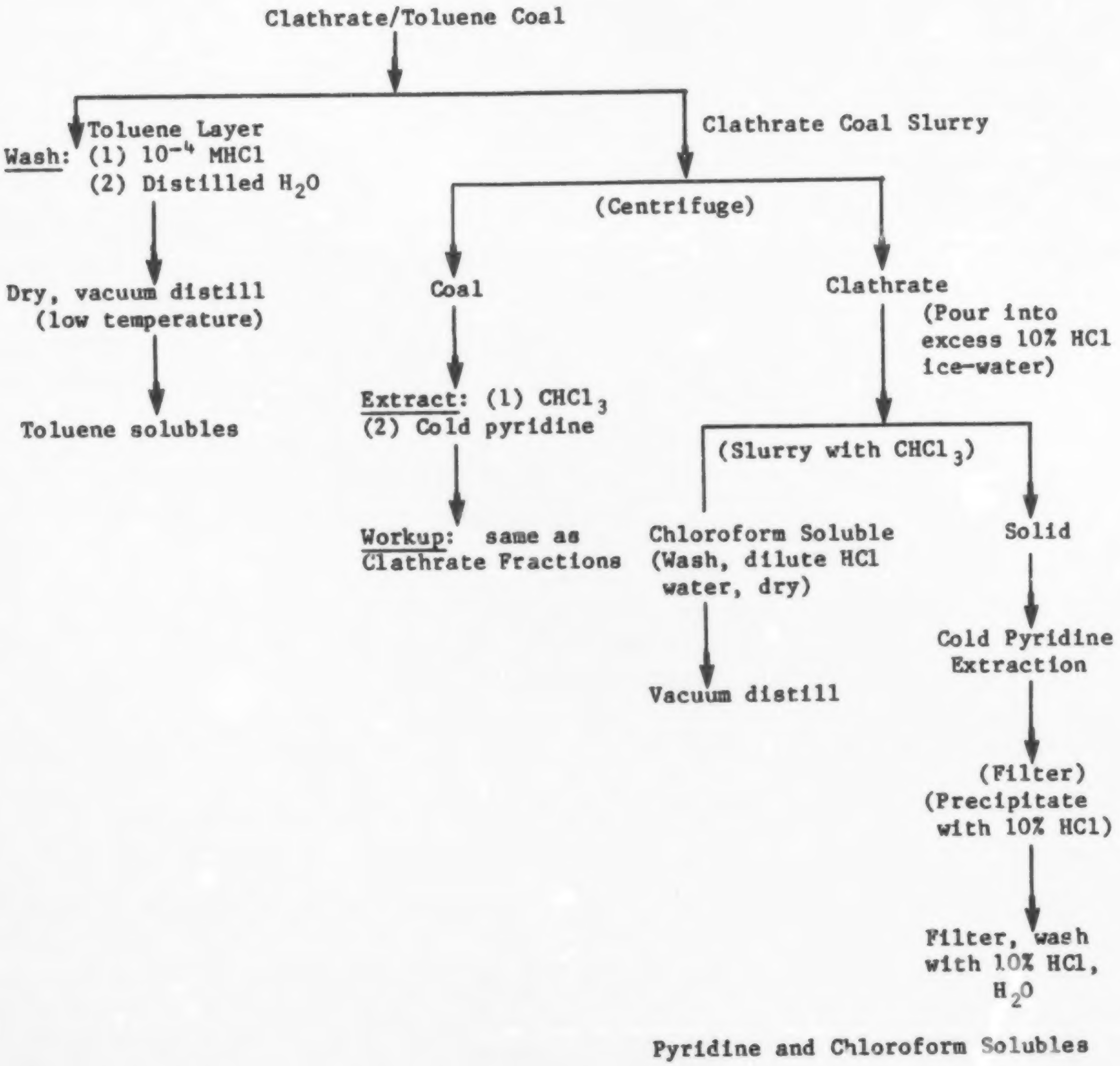
Table 8 – Catalytic hydrogenation ability of $RuCl_2(PPH_3)_3$ in liquid clathrate media[a]

Substrate	Quantity	Catalyst wt. (mg)	Ratio	Reaction[b]	Time	%hydrogenated[c]	%isomerized[c,d]	%unchanged[c]
1-octene	2 ml	100	123	Toluene 15 ml	20 hr	66	0	34
1-octene	0.5 ml	25	123	Toluene 15 ml	20 hr	100	0	0
1-octene	3 ml	0	—	—	20 hr	0	0	100
1-octene	3 ml	150	123	—	20 hr	60	28	12
1-octene	0.5 ml	25	123	—	4 hr	44	15	41
1-octene	0.5 ml	25	123	—	20 hr	75	19	6
Phenanthrene	0.5 g	25 mg	108	—	20 hr	0	0	10
1-octene	0.5 ml	25 mg	123	1.c., 15 ml no toluene	20 hr	97	3	0

a *all reactions conducted under ambient conditions*
b *15 ml $[NPr_4][Al_2Et_6I]$ nxylene liquid clathrate and 15 ml toluene unless otherwise noted*
c *as determined by G.C. integration*
d *identified as isomers of 1-octene via G.C./M.S.*

SCHEME

SEPARATION SCHEME


Clathrate/Toluene Coal
Toluene Layer
Wash: (1) 10^{-4} MHCl
(2) Distilled H_2O
Dry, vacuum distill
(low temperature)
Toluene solubles
Clathrate Coal Slurry
(Centrifuge)
Coal
Extract: (1) $CHCl_3$
(2) Cold pyridine
Workup: same as Clathrate Fractions
Clathrate
(Pour into excess 10% HCl ice-water)
(Slurry with $CHCl_3$)
Chloroform Soluble
(Wash, dilute HCl water, dry)
Vacuum distill
Solid
Cold Pyridine Extraction
(Filter)
(Precipitate with 10% HCl)
Filter, wash with 10% HCl, H_2O
Pyridine and Chloroform Solubles

SCHEME 1.

FIGURES

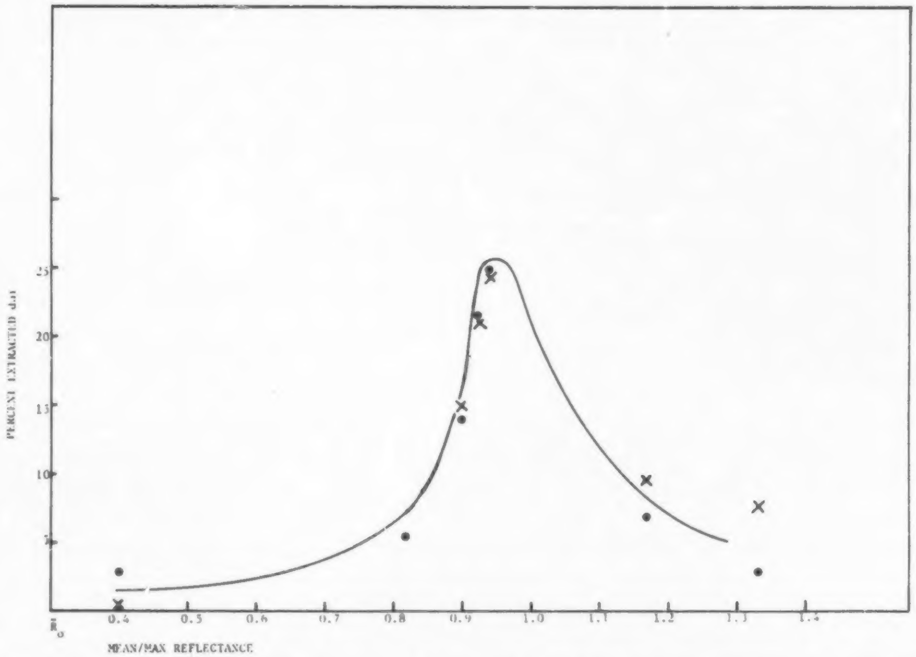


Fig. 1 – Coal extraction by refluxing pyridine (.) and by TETRA-N-PROPYLAMMONIUM-TRIETHYL ALUMINIUM CLATHRATE (x)

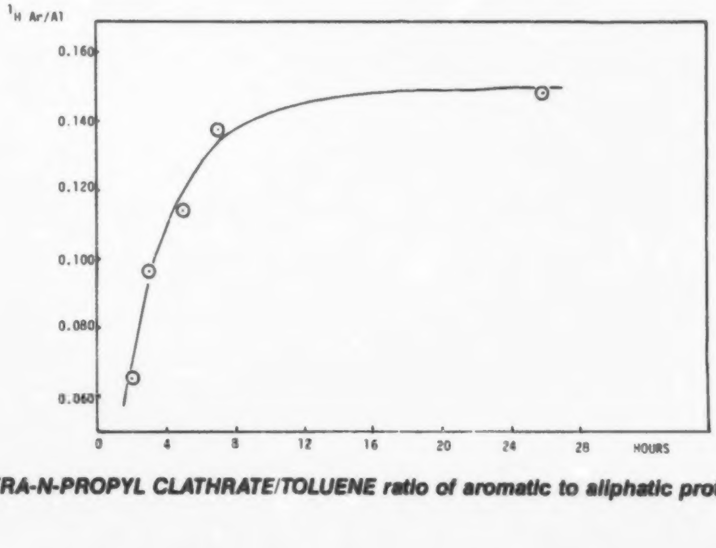


Fig. 2 – K-seam TETRA-N-PROPYL CLATHRATE/TOLUENE ratio of aromatic to aliphatic protons: toluene layer

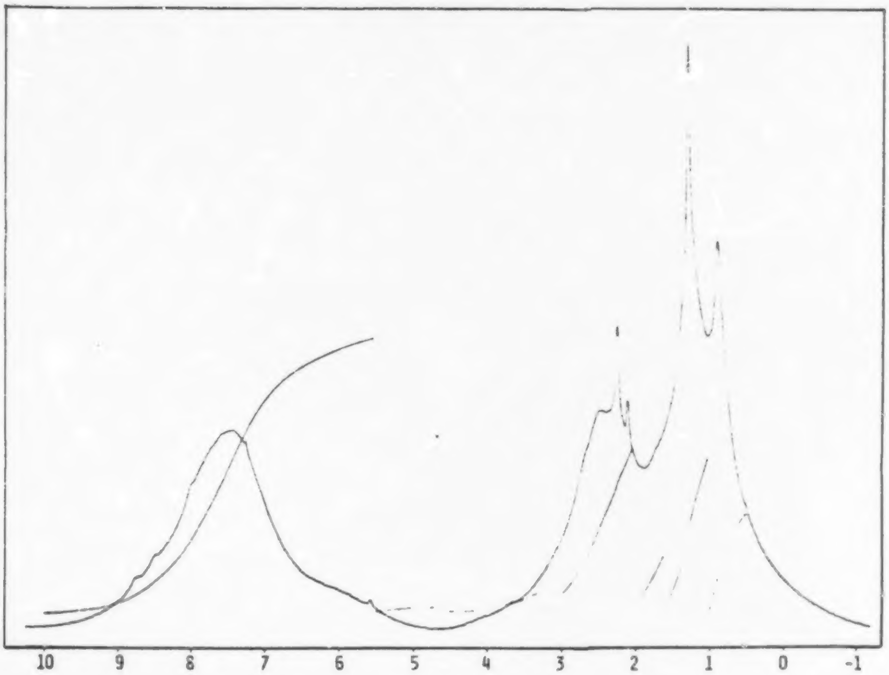


Fig. 3 – Proton NMR K-seam asphaltene $AsCl_3$ solution 0.005 m $Cr(AcAc)_2$ added for ^{13}Cmr

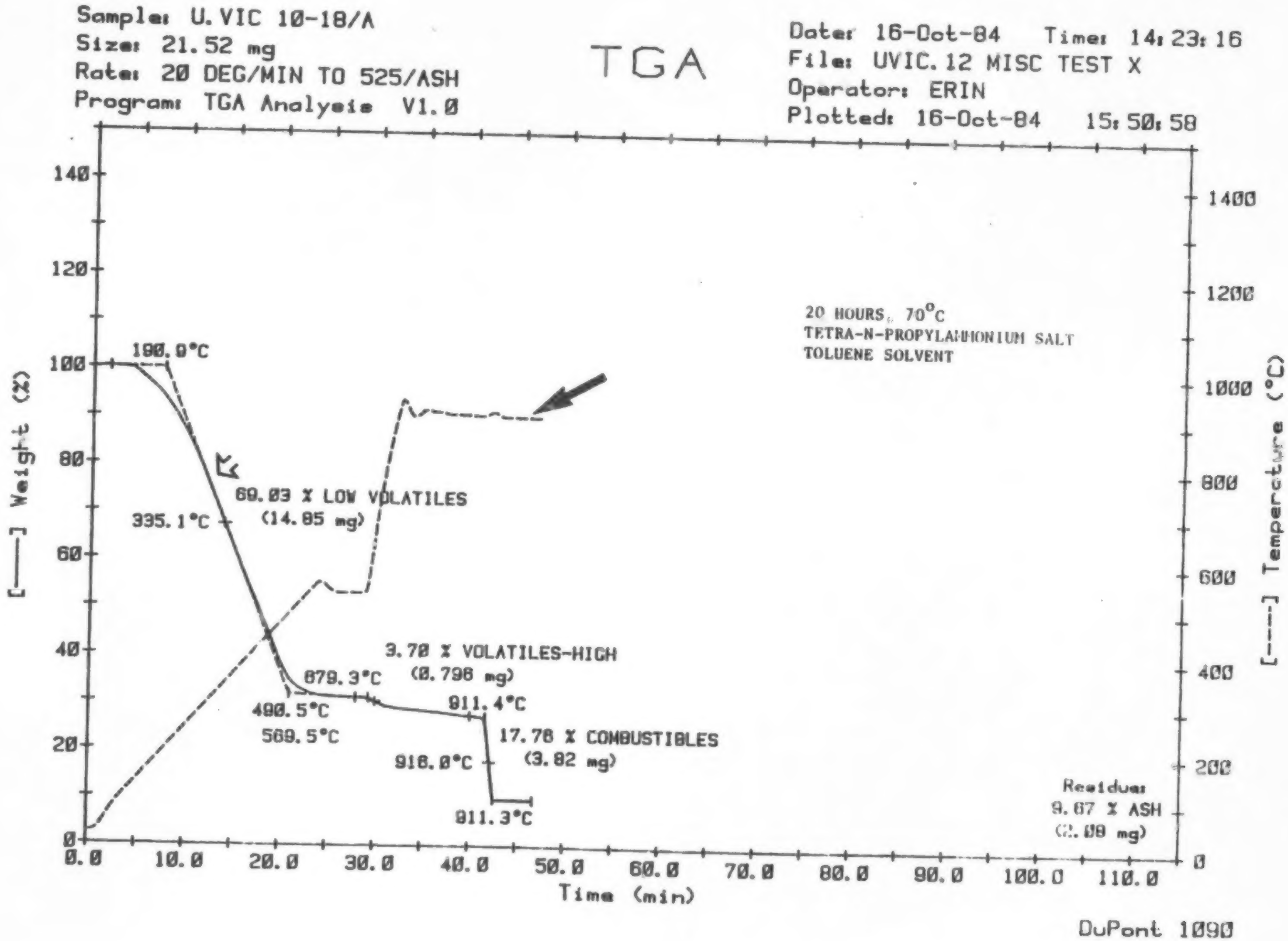


Fig. 4(a) – Toluene solubles fraction Devco clathration

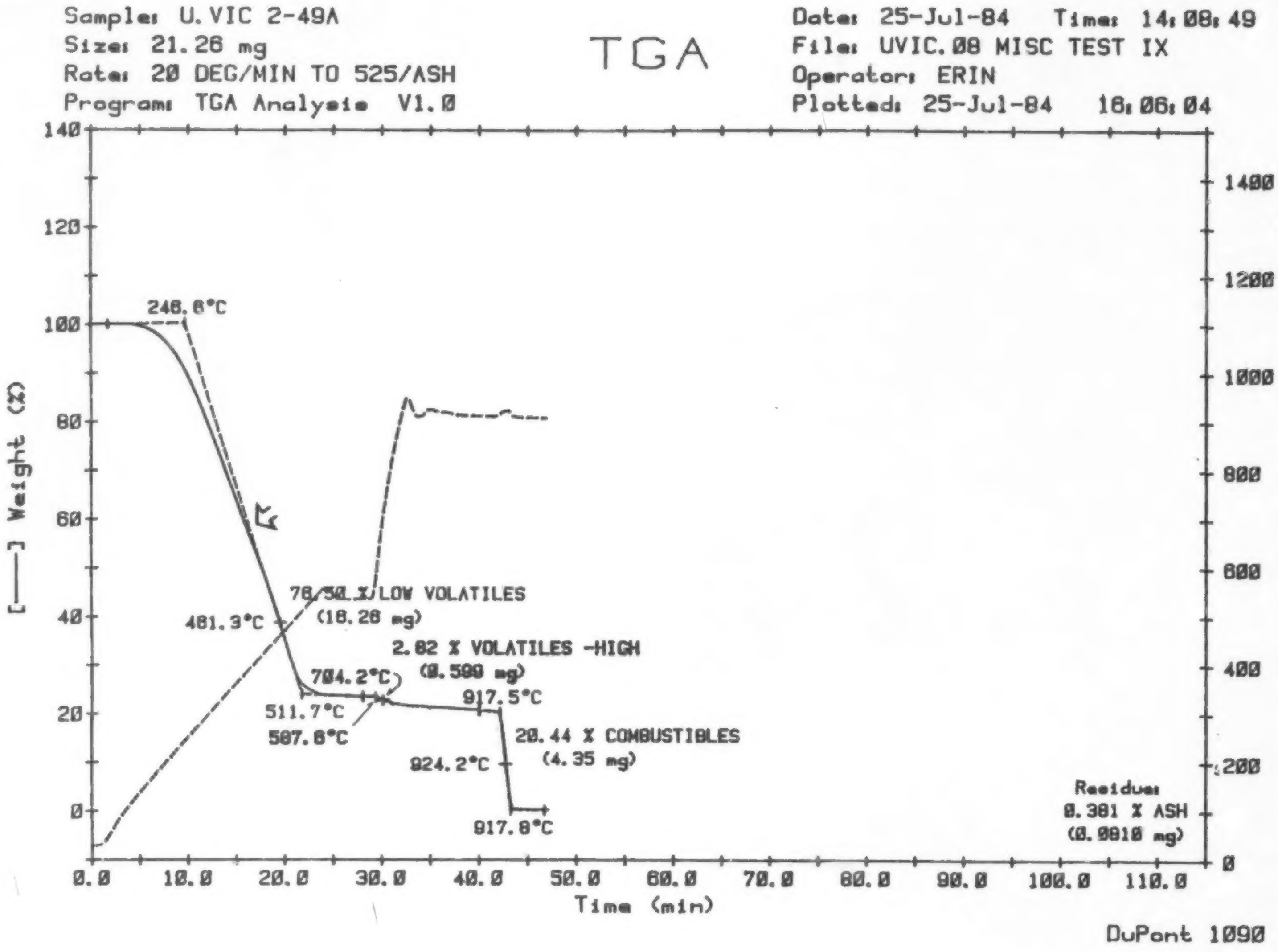


Fig. 4(b) – Toluene soluble fraction K-seam clathration

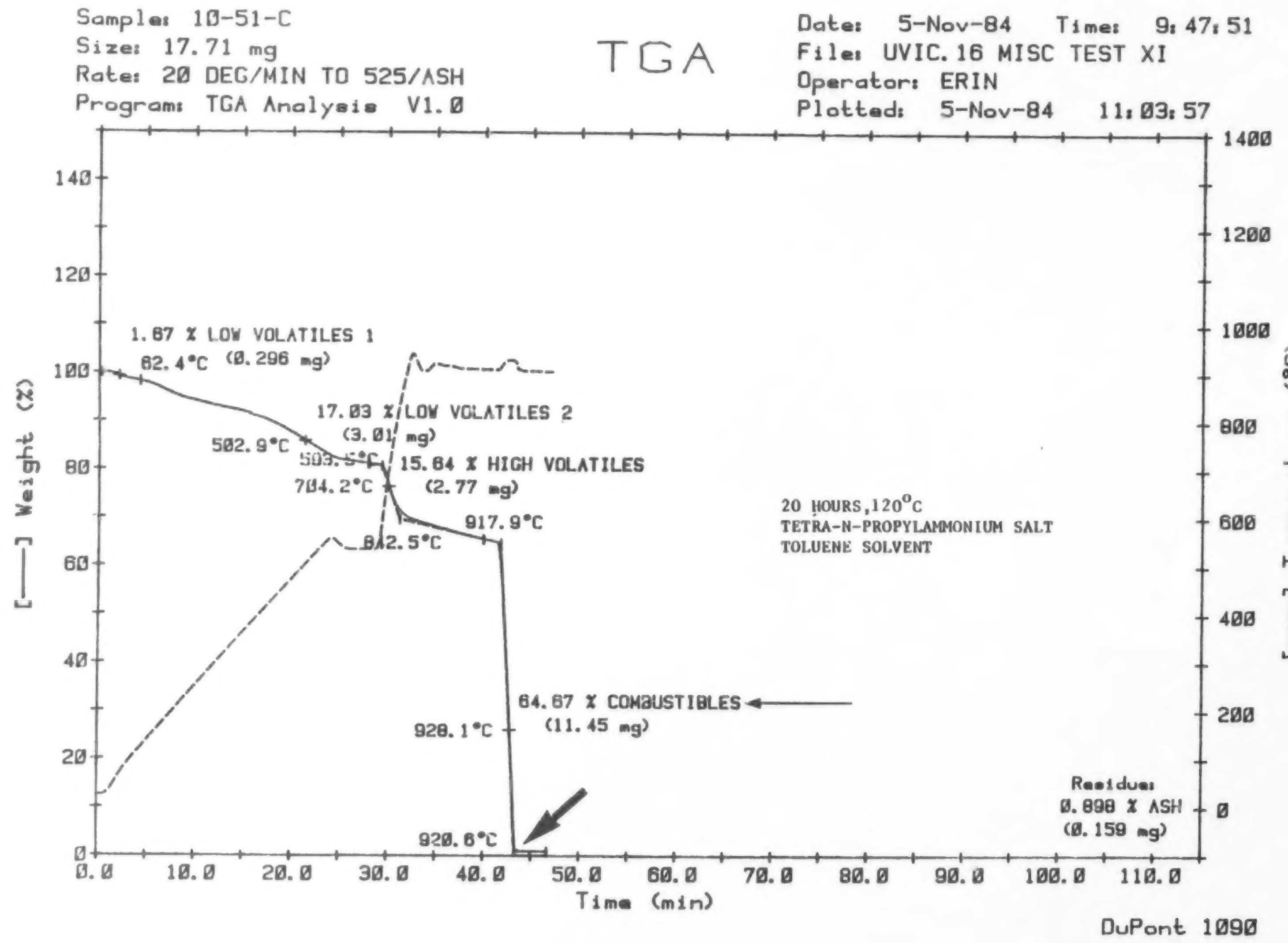


Fig. 5 – Pyridine solubles fraction Devco clathration

FIGURE 5 (a)

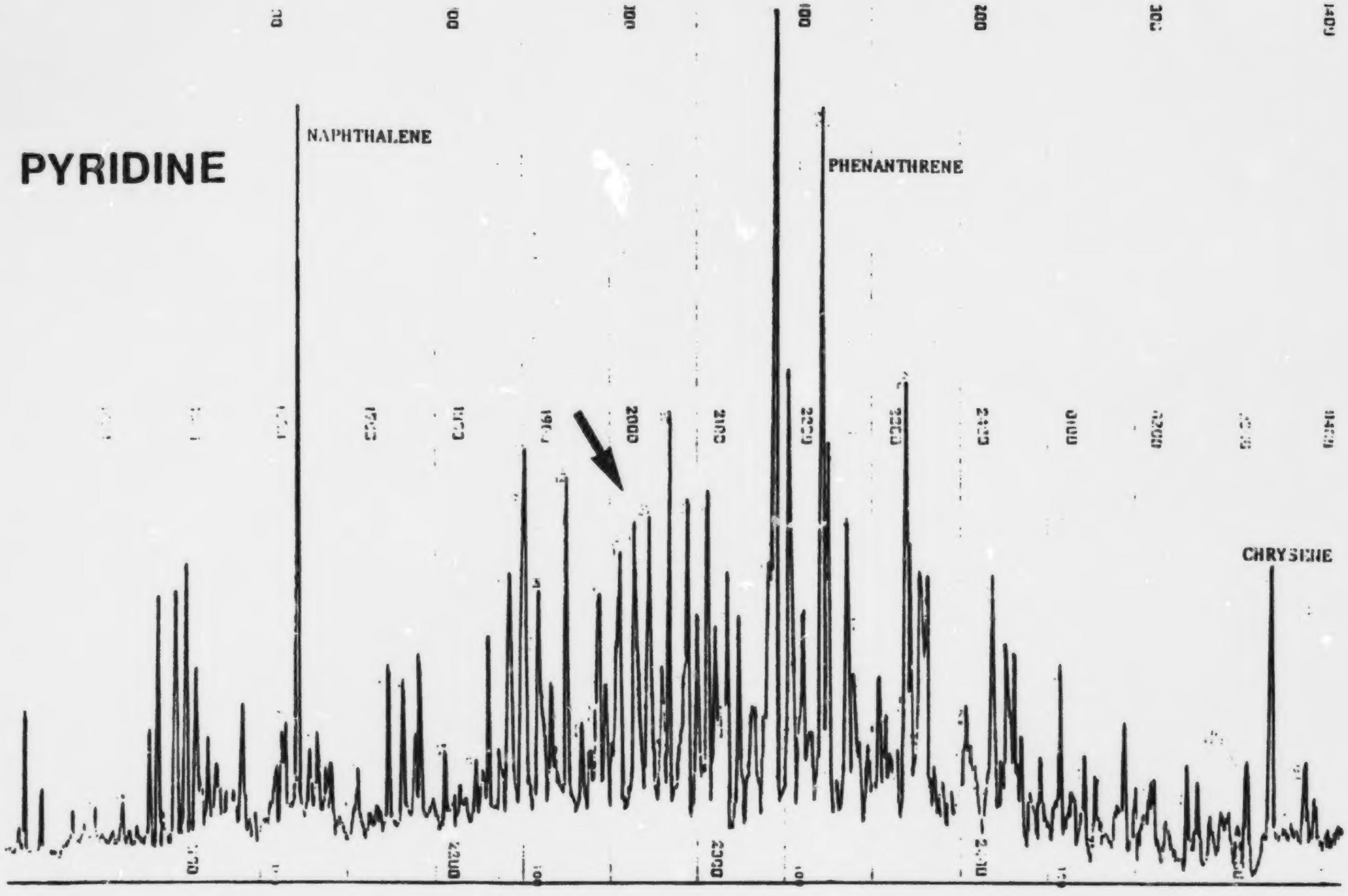


Fig. 5(a) – Sample 10-11-1-1 Toluene fraction DEVCO coal PYRIDINE REFLUX

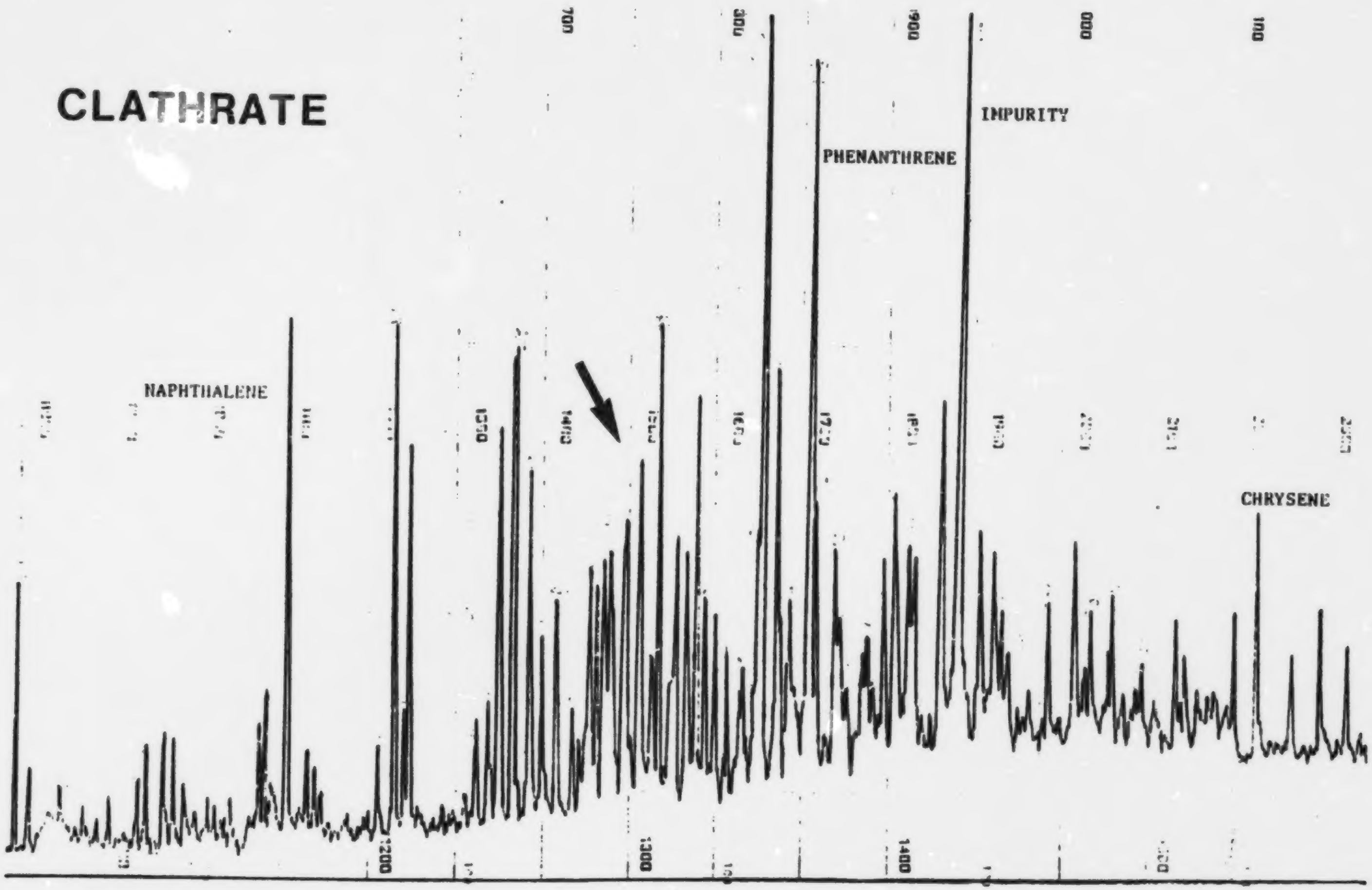


Fig. 5(b) – Sample 10-42-1-1 Toluene layer solubles METHANE CI

APPENDIX

MODIFIED BROWN-LADNER EQUATIONS

I. Schwager, Farmanian and T.F. Yen

$$f_a = \frac{\frac{C}{H} - \frac{H_\alpha^*}{x} - \frac{H_o^*}{y}}{\frac{C}{H}} = \text{fraction of total carbon which is aromatic carbon}$$

$$\frac{H_{aru}}{C_{ar}} = \frac{\frac{H_\alpha^*}{x} + H_{ar}^* + \frac{O-O_{OH}}{H}}{\frac{C}{H} - \frac{H_\alpha^*}{x} - \frac{H_o^*}{y}} = \text{ratio of substitutable aromatic edge atoms to total aromatic atoms}$$

$$\sigma = \frac{\frac{H_\alpha^*}{x} + \frac{O}{H}}{H_{ar}^* + \frac{H_\alpha^*}{x} + \frac{O-O_{OH}}{H}} = \text{fraction of the available aromatic edge atoms occupied by substituents}$$

$$R_s = \sigma C_A \frac{H_{aru}}{C_{ar}} = \text{number of substituted aromatic ring carbons}$$

$$n = \frac{H_o^*}{H_\alpha^*} + 1 = \text{number of carbon atoms per saturated substituent}$$

$$C_A = \frac{f_a (C)(M)}{100} = \text{total number of aromatic carbom atoms}$$

$$R_A = C_A \left(\frac{1 - H_{aru}/C_{ar}}{2} \right) + 1 = \text{number of aromatic rings}$$

C = mol % carbon

H = mol % hydrogen

O = mol % oxygen

O_{OH} = mol % phenolic oxygen

H_{ar}^{*} = mol fraction aromatic hydrogen (>5.0δ)

H_{α}^{*} = mol fraction hydrogen α to aromatic ring (<5.0 >1.73δ)

H_{o}^{*} = mol fraction of aliphatic hydrogen not α to aryl ring (<1.73δ)

x = average ratio of hydrogen to carbon on carbons α to aryl ring

y = average ratio of hydrogen to carbon on aliphatic carbons not α to aryl ring

Assumptions: All oxygen is attached to aryl rings in either phenol or aryl ether groups. All phenolic hydrogens found by the TMS derivative method are under the aryl absorption. $x = y = 2$.

Reference 6.

II. Bartle and Jones

$H_{\alpha}^{*} = \frac{H_{\alpha}}{H}$ where $H_{\alpha} = 2 - 3.3\ \delta$

replaces $H_{\alpha} = <5.0 >1.73\ \delta$

$H_{\beta}^{*} = \frac{H_{\beta}}{H}$ where $H_{\beta} = 1.0 - 1.6\ \delta$

replaces $H_{o} = <1.73\ \delta$

$H_{ar}^{*} = \frac{H_{ar}}{H}$ where $H_{ar} = 5.5 - 9.0\ \delta$ with assumption 60% of the hydrogen is phenolic

The Brown-Ladner approach is then applied with these modifications.

III. f_{a}^{*} = fraction of total carbon which is aromatic based on ^{13}C spectra.

Reference 6a.

As the partial listing shows, the two samples have a virtually identical pattern of fused (naphthalene) or linked aromatic rings (biphenyl); this is not unexpected for the coalification of K-seam. Subsequent families of alkylated aromatics revealed in both chromatograms include biphenyls (substituted with three and four saturated carbon units), alkylated dihydrophenanthrenes, alkylated phenanthrenes and anthracenes (three and four saturated carbon units), pyrene, dihydropyrene and their mono and dialkyl derivatives.

In addition, the computer search reveals the normal alkane series from $C_{11}H_{24}$ to $C_{20}H_{42}$ in both samples.

Table A.1 – Modified Brown Ladner analysis of the NMR spectra of pyridine soluble material from K-seam and Devco coals

	f_a			H_{aru}/C_{ar}		σ		η
Coal Sample	Bartle	Yen	f_a^*	Bartle	Yen	Bartle	Yen	Yen
2-47-B (K/Clathrate)	0.84	0.73	0.74	0.57	0.60	0.43	0.53	1.93
11-2-9 (K-Reflux Pyridine)	0.84	0.76	0.71	0.55	0.57	0.41	0.51	2.32
11-2-11 (K-Reflux Pyridine)	0.84	0.75	0.75	0.58	0.57	0.41	0.52	2.20
10-29-B (Devco/ Clathrate)	0.83	0.76	0.74	0.49	0.53	0.14	0.60	1.97
11-10-12 (Devco/ Reflux)	0.86	0.76	0.78	0.57	0.64	0.31	0.37	2.59

Definitions: F_a = *fraction of total carbon which is aromatic carbon*
H_{aru}/C_{ar} = *ratio of substitutable aromatic edge atoms to total aromatic atoms*
σ = *fraction of available aromatic edge atoms occupied by substituents*
f_a^* = *fraction of total carbon which is aromatic, ^{13}Cmr*
η = *number of carbon atoms in average alkyl substituent*

Table A.2 – K-Seam Coal
Volatile constituents from isolation
(a) Toluene reflux
(b) Toluene extraction of clathrate phase

Aromatics* (Order of elution, partial listing)

	Reflux (11-2-0-1-1)	Clathration (2-56-11)
1.		tetralin
2.	naphthalene	naphthalene (standard)
3.	2-methylnaphthalene	2-methylnaphthalene
4.	1-methylnaphthalene	1-methylnaphthalene
5.	biphenyl	biphenyl
6.	2-ethylnaphthalene	2-ethylnaphthalene
7.	2,6-dimethylnaphthalene	2,6-dimethylnaphthalene
8.	2,7-dimethylnaphthalene	2,7-dimethylnaphthalene
9.	1,3(1,7)-dimethylnaphthalene	1,3(1,7)-dimethylnaphthalene
10.	2,3(1,4)-dimethylnaphthalene	2,3(1,4)-dimethylnaphthalene
11.	1,2-dimethylnaphthalene	1,2-dimethylnaphthalene
12.	methylbiphenyl	methylbiphenyl
13.	isopropylnaphthalene	isopropylnaphthalene
14.	dibenzofuran	dibenzofuran
15.	C-3 naphthalene (3 peaks)*	methyldiphenylmethane*
16.		C-3 naphthalene*
17.		methyldiphenylmethane*
18.	2,3,6-trimethylnaphthalene Fluorene	2,3,6-trimethylnaphthalene Fluorene
19.	C-3 naphthalene*	C-3 naphthalene*
20.	3,3′-dimethylbiphenyl	3,3′-dimethylbiphenyl
21.	C-4 naphthalene*	C-4 naphthalene*
22.	C-4 naphthalene*	C-4 naphthalene*
23.	4,4′-dimethylbiphenyl	4,4′-dimethylbiphenyl
24.	C-4 naphthalene*	C-4 naphthalene*
25.	C-4 naphthalene*	C-4 naphthalene*
26.	2,2′-dimethylbiphenyl	2,2′-dimethylbiphenyl
27.	2-methylfluorene	2-methylfluorene
28.	1-methylfluorene	1-methylfluorene

** Unconfirmed or unknown isomer*
Numbering indicates approximately equivalent retention index

SESSION III

DISCUSSION

MODERATOR: D. ABBOTT, RESEARCH AND PRODUCTIVITY COUNCIL, N.B.

CLARK (ALBERTA RESEARCH COUNCIL): I have a question for Dr. Stobart. Your attempts to catalyze hydrogenation of things like octane with rhodium catalysts seemed to work reasonably well, but I notice that the phenanthrene ring system was unreactive. Since we're dealing with highly aromatic compounds in coal liquids, do you really think that area is worthy of further pursuit?

STOBART (UNIV. OF VICTORIA): That's a very good question and I must compliment the questioner on his powers of observation. We saw no hydrogenation of that system. We would not expect this from a ruthenium catalyst of the type that was used in the system. This is primarily a hydrogenolysis catalyst and I ought to make two points, I think, in trying to answer this question. The first is that if we were to use a catalyst that would hydrogenate aromatics sufficiently as a primary step, then this would effectively destroy our clathrate system which relies for its sustenance on the inclusion of an aromatic molecule. In other words, to take the example we have been using, in a toluene clathrate, if we hydrogenate the toluene, this is not really what we want to do.

The second point I would like to make is that the bonebreaking processes in coal mobilization may well be associated more with hydrogenolysis than with direct hydrogenation of arene systems, and it seems to us that if we can mobilize the coal into smaller polyaromatic fragments then we can look at hydrogenation of those fragments subsequently. The main objective is to use hydrogenolysis to break up the coal mass.

CLARK (ALBERTA RESEARCH COUNCIL): A followup question to you, Dr. Stobart, concerning your use of aluminum chloride or the super acid systems. It's quite well known that these super acid systems react very quickly with aromatic organo-sulphur compounds, and since most of our bituminous coals do indeed contain these sorts of molecules, I am wondering whether you had thought about that and whether you would consume quite a bit of aluminum chloride in just trying to satisfy the aromatic organo-sulphur compounds in the coal liquids?

STOBART (UNIV. OF VICTORIA): I think that is a very good point. I think that in the worst possible scenario what we would see would be stochiometric consumption of aluminum chloride which is clearly not what we want. Inherent in Atwood's observations on liquid clathrates is the discovery that certain of the aluminum-containing components in the clathrates are in fact alkyl polyaluminum halide species. We feel that these species may not be so susceptible to the kind of reaction that you have been describing and that the activity of such species in relation to hydrogenation and dismutation is something that is worth investigating.

CLARK (ALBERTA RESEARCH COUNCIL): I would like to address a few simple inquiries to Judith Potter concerning liquefaction in bitumen with hydrogen sulphide and hydrogen. I don't think you put experimental details on your graph for these particular experiments and the questions I would particularly like to ask concern the actual percentage of coke formation from the coal and the bitumen and at what temperatures you are making these liquefaction experiments?

POTTER (UNIV. OF REGINA): Well, in the first instance we are not responsible for conducting the experiments and the experimental details are not available at this time. So I'm afraid that I can't allude to experimental conditions. With regard to the first part of your question, I think what you're asking me, is there semicoke formation in both the coal-derived solids as well as the bitumen-derived solids? The answer is yes, there is. In general there is a larger proportion of semicoke formed from the bitumen than there is from the coal.

YAN (MOBIL): I have a question for Dr. Scott. As you pointed out, one of the important things about pyrolysis is to be able to utilize the chars effectively. I was wondering if you have more information on characterizing the chars? I can mention that there are several studies at Princeton University on high temperature, very short time pyrolysis on screens and by Martin Hartburg at the Bureau of Mines in Pittsburgh using lasers. I am talking about the physical structure changes of the char. Now the real question I wanted to ask about is the effect of entrained oxygen compounds on the properties of the char? How do they affect the physical structure?

SCOTT (UNIV. OF WATERLOO): Firstly, no, we haven't really investigated the physical structure of the chars although this is on our agenda for future work. I agree with you. It's very important if you want to have the whole pyrolysis process work. You must be able to supply information about the combustion characteristics of the chars. All we know at the moment is that the chars from fast pyrolysis processes are more reactive than the parent coals. In every case, particularly with the low-rank coals, they are extremely reactive to the point where they can be pyrophoric. So we expect to find a very high degree of reactivity in these chars relative to parent coals. As far as your second question about oxygen, I'm not quite sure what you mean. Are you speaking of the need to supply heat for the pyrolysis process and therefore you must burn some of the in situ material?

YAN (MOBIL): That's correct, you must burn some of them and some oxygen would be entrained into the next stage when you try to do hydropyrolysis. That's what I think.

SCOTT (UNIV. OF WATERLOO): Well, I wouldn't agree that it's necessarily so. There are many ways of supplying heat in the process and it doesn't have to be supplied by direct in situ combustion. It can be supplied by some kind of precombustion or from flue gases. There are many possibilities and while in situ combustion is convenient, I wasn't aware that this would have a profound effect on the char form, but it may be worth investigating.

YAN (MOBIL): Dr. Potter, I need some education because I don't know much of anything about the significance of petrographic analysis. First of all in your product, how come you produce so much of the isotropic material? What is the significance of that? Secondly, why in the world do you find unaltered coal in such drastic conditions and especially the low-rank Onakawana coal?

POTTER (UNIV. OF REGINA): In answer to your first question regarding the significance of the isotropic material, the material which we refer to as semicoke is optically anisotropic. The material which is not anisotropic, the isotropic material to which you refer, is a product of the liquefaction process and it is derived directly from coal macerals which may or may not have undergone some alteration. The degree of alteration we can measure in terms of the increase in reflectance of those isotropic materials. For example, in some of the slides I showed isotropic material which due to perhaps low temperature conditions had only a marginal increase in reflectance.

An instance I recall is perhaps the change in reflectance from that of a subbituminous coal maceral at say .43% reflectance to .89% reflectance. One would assume from that a relative increase in carbon content and measuring the reflectance shows that there has been some chemical alteration of that material. The chemical alteration may not have gone to completion by producing either highly reflective char, which is not going to give you any more volatile material or liquid products, nor has it become optically anisotropic to produce an insoluble semicoke. So you also have to look at the isotropic material to judge if it is still liquefiable or whether it will produce a char.

YAN (MOBIL): Oh, I had a misconception because in the oil industry we make coke from heavy residual oils. Here we talk about the precursor of coke in the mesophase and after heating the mesophase, the coke. When we talk about isotropic material we mean we have a chance of making needle coke which is isotropic and makes a very good electrode. I thought maybe you had found a good way to make needle coke.

POTTER (UNIV. OF REGINA): Well, I don't think you'll make needle coke very well from these materials. I think the one difference here between liquefaction and carbonization is that only under certain pyrolysis conditions or using certain pyrolysis systems, can you produce the high temperature coke which I distinguish from the lower temperature coke or semicoke which is the most common product of coal hydrogenation and other lower temperature coal liquefaction systems. We have only seen the high temperature coke from relatively high-rank coals, in this case, high-volatile bituminous coals, specifically the Fording coal.

LEE (IREQ): I have a question for Dr. Sears. In both of these pyrolysis processes discussed today, the yield of product and product distribution seems to correspond very closely with the old town-gas process. I would like to know what significant improvement we have over the old town-gas process?

SEARS (CANMET): Well, we've barely got started on the experimental part of our work. I think you'll find that the Brookhaven people manage to get better yields than the town-gas process and I see no reason to suppose that we cannot as we get going. I will be happy when we get better analysis results than we've had so far.

SCOTT (UNIV. OF WATERLOO): I think in some respects our pyrolysis process is very similar to the town-gas process if you used a counter-current moving bed. Then you accomplish a pyrolysis reaction in the upper part of the bed and generate tars. But that's a relatively uncontrolled kind of pyrolysis and the tar yields are generally very low. In the case of flash pyrolysis or hydropyrolysis, it's a controlled pyrolysis with controlled residence times, controlled temperatures and the tar yields are significantly higher.

NILL (ALBERTA RESEARCH COUNCIL): First of all Mr. Moderator, I would like to make a point of clarification on work that we've done in coal pyrolysis. It was mentioned by one of the speakers or neglected by one of the speakers that we had worked in this area. I would like to say that we've conducted flash pyrolysis experiments since 1982 and flash hydropyrolysis experiments in the last year and a half with an experimental apparatus similar to that used in Dr. Sears' work. First of all, one of the major conclusions that we have reached in our work is that the hydrocarbon yield does not increase above 650°C except for relatively minor quantities of methane for subbituminous coals in flash pyrolysis. I'd like to ask Dr. Scott if he observed the same trend, since he reports tar yields decreasing? Did he also see a corresponding increase in hydrocarbon gas yields?

SCOTT (UNIV. OF WATERLOO): Yes, indeed we did and the maximum for the lower rank coals, the points at which we obtain maximum liquid yields, was always between 600 and 650°C. On one of my slides that I glossed over, there were Alberta Research Council results, I might add.

NILL (ALBERTA RESEARCH COUNCIL): That's very encouraging to hear. The second point I would like to make is something that Dr. Teo alluded to about the quality of tar products. We have found that at lower temperatures, and we work as low as 550°C in flash pyrolysis, our products are very highly substituted with hydroxyl and aliphatic groups. We get up to three hydroxyl groups on a single benzene ring and at higher temperatures we're simply removing those and creating more water in our products. As for the other compounds such as nitrogen and sulphur substitution in heterocyclic compounds we find that they're stable in the coal tars up to 800°C. I'd like to point out from an economic point of view, when we consider tar quality, that it's very important that we have some way of upgrading these compounds. We've achieved this by using high-pressure hydrogen hydropyrolysis. We're able to crack our tars almost completely producing benzene as the major product. I wanted to make that point because often tar yields are recorded and considered most significant whereas we find, as concluded by Dr. Scott, that we aren't doing anything more to tars above 650°C than removing some components to give a useful product. Maybe I should give you a chance to comment on that.

TEO (UNIV. OF BRITISH COLUMBIA): I also came to the same conclusion as Dr. Scott. We also observed the maximum tar yield in the region between 500 and 650°C under our pyrolysis conditions.

NILL (ALBERTA RESEARCH COUNCIL): The last point I'd like to make is in reference to char reactivity experiments. First of all I'd like to say that we're starting a rather significant program in that area including actual combustion of pyrolysis and hydropyrolysis chars in a self-sustaining flame. Many people have reported on char reactivity and they use the TGA experiment. I'd like to clarify that low-temperature reactivity only gives you a portion of information. The reaction mechanisms which are occurring at the temperatures used in TGA may be very different from those which occur in a flame. In the past it has been characteristic of utility companies to ignore some of these low-temperature experiments and indeed concentrate on volatile matter content because these analogies aren't made. I'd like to say that volatile matter in the preliminary work that we've done on combustion of pyrolysis char does not seem to be important even at much higher temperatures. A great deal more work has to be done in this area with reference to surface area development and reactivity.

I'd like to ask about the conclusions made by Mr. Royce on CO_2 reactivity with some of the demineralized chars. Did you study the surface area of those chars in order to make conclusions as to the reactivity on a surface area basis as opposed to a weight basis?

ROYCE (UNIV. OF WATERLOO): Sometimes removing the minerals from the coal can increase the surface. Removing the minerals from the coal can also act as a hinderance to the reaction as well, depending on the rank of the coal. It has been found that removing the minerals from higher rank coals, in fact, increases the reactivity so there has to be a compromise between surface area effects and catalytic effects.

MONNIER (CANMET): I have a question for Dr. West. Do you have degradation of clathrate with time? I'm not familiar with this so I was wondering whether you could reuse clathrate? That is, have you cycled another charge of coal through the same clathrate phase?

WEST (UNIV. OF VICTORIA): This is a project which is in progress and we've been defining the limits of it in that way. The clathrate does not degrade in contact with the coal over the time that we heat it. Of course we break it up after that, and in particular, when we do try the lignite or subbituminous coals and put them in contact with the clathrate, the clathrate phase darkens to some extent. There is very little passage of material into the toluene in the standard reaction as you might expect. But then, by the same token, the surface oxidation of those lower rank coals does not destroy the clathrate phase. It's not degraded by the phenolics and the acids that are on the surface of the coal. I suppose that you can reuse the clathrate as a working phase. I don't know why you would actually want to isolate it and reuse it.

MONNIER (CANMET): Well, you have three phases in your system. You have coal, you have clathrate and you have solvent. I was thinking if you have a process in the first reactor, you would have clathrate and coal and you take the clathrate and you send it to another reactor where you would have a solvent and you have to remove the inorganic material.

WEST (UNIV. OF VICTORIA): I understand now what you're saying, and I think that you can do that by fractional crystallization of salt. We did not want to do the complicated work with salts. We're not working with systems that are easily fractured out in that way. So we haven't tried to recover the total salt in our system but potentially that could be done by just crystallizing it out.

JOHNSON (DEPT. OF MINES AND PETROLEUM RESOURCES, B.C.): Maybe I could just add to what Paul said about that. We had the Hat Creek and Forestburg samples exposed to the clathrate in a closed system for several months and didn't see any degradation in the clathrate.

ABBOTT (RESEARCH AND PRODUCTIVITY COUNCIL, N.B.): Dr. Teo gave us a fine exposition of characterization of tars and liquids. Will this work be continuing to char characterization which has become most topical?

TEO (UNIV. OF BRITISH COLUMBIA): The char characterization at this stage includes only TGA analysis because, as you know, the char is one of the end use products. You should have some way to characterize them like carbon content, volatile matter and inherent ash properties that might affect the burning character of the char. Also, some other physical measurements such as pore-size distribution and surface area measurements are also essential. At least our TGA analysis gives some kind of picture as to what per cent of the volatile material may be stripped from the parent coal, and what will be the quality of the char for combustion. I think physical and chemical characterization are both important in this area.

HODD (SBRG): I would like to direct a question to Paul West. It seems to me that the clathrate system has some novel features, but I have some questions regarding what the true economic benefit might be. It seems to me there is a very small margin of improvement to bring down the cost of producing liquid fuels from coal. You've got a certain cost in terms of coal, and a certain amount of hydrogen stochiometrically to put into the products. You have to build the plant to handle coal and so forth. It seems to me that the substitution of operating at low pressures and temperature comes at the expense of having very long residence times and therefore very large reaction vessels and piping and so forth. Where do you see the key significant benefit of this development to be? Where is the breakthrough likely to lie? I'm just having trouble visualizing where the benefit is going to lie with this technological advance.

WEST (UNIV. OF VICTORIA): Your points are very well taken. At the present the straight physical dissolution as a working phase is not economic per se as a physical medium for dissolving coal. The projection of its economic vitality is strictly in terms of whatever catalytic or chemical agents you can introduce into that clathrate phase in order to significantly break down the coal, either to achieve de-ashing or for removal of sulphur to produce a product which you can upgrade subsequently. It requires that kind of advance to render it competitively economic in any real sense. There is a range of studies in progress in the United States, as well as here, which is directed at this kind of low-temperature depolymerization of coal and there is a series of papers coming out of California by Dr. Ola who is a super acid authority. Using borontrifluoride, hydrogen and hydrogen fluoride, extremely high conversions of coal at low temperature (up to 60 or 70%) employing hydrocarbon hydrogen and hydride transfer agents are achieved. We would see the compatibility of our system with Lewis acids as having a parallel with that and we would not foresee no possibility of us achieving the same kind of depolymerization mechanism in the working phase, with the added advantage of being able to remove the material continuously into a stripping phase. That is a long answer to your question. I do think that we need a significant advance in terms of that depolymerization reaction before we are at all competitive with the high-temperature processes.

HODD (SBRG): I understand what you're saying then. You look at a fundamental change in the characteristics of the primary products before going to a subsequent upgrading-type process.

WEST (UNIV. OF VICTORIA): We do believe that we must have a depolymerization step, be it a hydrogen transfer or be it an ionically mediated depolymerization, in order to get more material into the working phase. The subsequent upgrading would be subject to the development of another process. That is also true in large measure with any of the other depolymerization approaches such as super acid decomposition of coal.

HODD (SBRG): Regarding pyrolysis, have any of the speakers any comments to make with respect to the environmental characteristics of some of the tars and what's been going on in the way of research to address how they can be safely used in the context of a source of liquid fuels. I know there is a great deal of concern with the hydrogenation products. I think one of the Japanese speakers yesterday indicated that a significant part of their ongoing work is environmental characterization to make sure that coal liquid products are environmentally and socially acceptable. What programs are going on in respect to the tar products that come out of pyrolysis operation?

SEARS (CANMET): I think you can safely say that virtually all of these heavy tars are going to be quite dangerous. They're going to contain polycyclic aromatics amd most of those things should be viewed with some caution. I think you're going to have to hydrogenate them all or hydrocrack them before they can be safely used. I think that can apply virtually for any of these heavy materials.

SCOTT (UNIV. OF WATERLOO): For the atmospheric pyrolysis tars made by the Australians, they have a process, which they are building into a demonstration-scale plant now, that very successfully hydrogenates and upgrades these tars.

HODD (SBRG): Would you have any information on the amount of hydrogen consumption which would be going into these materials?

SCOTT (UNIV. OF WATERLOO): No, I haven't. I haven't seen any publications on this as yet.

SESSION IV

GASIFICATION

Chairman: T.D. Brown

SESSION IV: PAPER 15

THE SPOUTED-BED COAL GASIFIER

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ABSTRACT

Development of the atmospheric pressure spouted-bed coal gasifier is described. The flexibility of the spouted-bed gasifier is illustrated with data from operation with different western Canadian coals, with dry ash versus agglomerating ash mode, with air/steam and oxygen/steam blasts, and with beds consisting of char or inerts. Internal gas composition and temperature profiles are presented to elucidate the behaviour of the gasifier, and the zones of combustion and gasification are mapped for both air/steam and oxygen/steam gasification. Some comparisons of the spouted-bed gasifier with other gasifiers are made.

**denotes speaker*

PRÉSENTATION 15

LE GAZÉIFICATEUR DE CHARBON À LIT À JET D'AIR

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RÉSUMÉ

Cette communication porte sur la mise au point du gazéificateur de charbon à lit à jet d'air, exploité à la pression atmosphérique. Elle présente les résultats de l'exploitation en mode sec et en mode d'agglomération des cendres, avec des jets d'air/vapeur et d'oxygène/vapeur, ainsi qu'avec des lits inertes et des lits de charbon. La composition des gaz du lit ainsi que les profils de température ont été mesurés dans le jet d'air et dans l'anneau en vue de délimiter les zones de combustion et de gazéification dans le lit à jet d'air. Des comparaisons entre le gazéificateur de charbon à lit d'air et d'autres types de gazéificateurs sont présentées.

**indique le conférencier*

THE SPOUTED-BED COAL GASIFIER

INTRODUCTION

The spouted-bed coal gasifier has been under development at the University of British Columbia for the past several years (1-3). This reactor has been shown to be a reliable and versatile system for gasification of Canadian coals. Table 1 shows the range of operating modes that have been tested in our experimental studies.

A comparison of the spouted- and the fluidized-bed gasifier has also been made (3). A number of western Canadian coals have been gasified. Table 2 lists proximate analyses of all the coals tested. Except for Klimax coal, which gave problems due to the high level of sodium in the ash that resulted in bridging between the silica particles of the inert bed, all coals have been successfully gasified. Tests with Klimax coal in a char bed presumably would not suffer from this problem. When the experiments with Balmer rejects containing 55% ash were done, a bed overflow line was lacking and hence the ash accumulated in the bed. The conditions therefore were not indicative of true steady state, and the results may have been affected. As is evident from Table 2, coals with moisture contents from 1.1. to 27%, ash levels of 4-55.6%, fixed carbon from 28.3-67%, and free-swelling index from 1 to 7 have been successfully gasified.

The above coals have been treated in gasifier tests lasting up to 15 hours, but for most experiments the tests last about 3-5 hours at steady conditions. N.K.K. of Japan are also developing an atmospheric pressure spouted-bed gasifier (4) which is based on operation in the agglomerating ash mode, and utilizes an additional combustor to get satisfactory carbon utilization values.

In this paper the performance of the spouted-bed gasifier is reviewed, with results covering a range of operating conditions and modes. Some recent test data are presented where successful operation in ash-agglomerating and catalytic modes are illustrated; however, these areas require further work for substantiation of the results. Probing of internal gas composition and temperature profiles has permitted the oxidizing and reducing zones of the gasifier to be delineated, and has added significantly to the understanding of how the spouted-bed gasifier works.

EXPERIMENTAL

The existing 0.3 m diameter unit built under contract is used throughout the work. Detailed descriptions are given elsewhere (2,3,5) and only a brief description will be presented here.

Coal is pneumatically transported using air or oxygen into the bottom of the reactor through a 31.8 mm inlet orifice (Fig.1). The remaining constituents of the blast which may be steam, air, or oxygen are injected into the reactor at the same location.

Hot gaseous products with some entrained coal fines leave the top of the gasifier and pass through two cyclones. In a number of selected runs, char from the first cyclone was recycled into the reactor via a rotary valve, entering at a single point in the reactor wall with some conveying air. Gases are cooled in three double-pipe heat exchangers and pass through a knock-out drum and filter before being fed to an incinerator.

RESULTS

In gasification the responses of interest in the process include:

a. heating value of the gas, G.H.V. (MJ/m^3), which is calculated from the heats of combustion of the hydrogen, carbon monoxide and methane present in the gas

b. gas yield from the coal, G.Y. (m^3/kg), which is defined as the total dry gas volumetric flow rate leaving the gasifier referred to S.T.P. divided by the M.A.F. coal rate

c. the efficiency factor – the product of (a) and (b) which, if divided by the heating value of the coal, is the cold gas efficiency of the gasification process: η_{cold} = G.H.V. * G.Y./C.H.V.

d. carbon conversion to CO, CH_4 and CO_2.

The effects of some of the gasifier operating parameters for air/steam gasification of coal are discussed below.

Air-Steam Gasification

For a given coal and mode of operation, two prime variables are used in the gasification experiments – the coal feed rate, and the air rate. The steam rate may also be adjusted, although the lower rank coals require no steam, because of their contained water. If the air rate is set at some multiple of the minimum spouting velocity of the inerts in the bed and the coal feed rate is varied, the gas heating value goes through a broad maximum as shown in Figure 2. An increase in coal feed rate beyond a critical value causes the reactor to cool, and the coal to accumulate. Eventually the reactor will choke. If the air rate is changed, the heating value curve in Figure 2 will shift. This is shown indirectly in Figure 3 where at a fixed coal feed rate, the heating value decreases linearly with increases in the air-to-coal mass ratio.

The gas yield is also a function of both air and coal rates; however, its behaviour is more simply described. Figure 2 shows that at a constant air rate, even where the heating value goes through a maximum, the gas yield decreases in approximately a linear manner with the increase in coal feed rate. Figure 3 shows that over the range of interest, a linear increase in gas yield results from increases in the air/coal ratio.

Since the air/coal ratio is the most common variable used in comparing gasification conditions, most results are presented in plots versus this ratio. The coal feed rate has been accounted for in an empirical manner suggested by the plots of Figures 2 and 3.

Examination of the experimental data showed that plots of heating value versus air/coal ratio showed considerable scatter due to differences in coal feed rate; however, the heating values-feed rate product yielded a smooth curve when plotted versus air/coal ratio. Figure 4 shows plots of the heating value-feed rate product and the gas yield/feed rate ratio versus air/coal ratio for all runs taken over three years with Forestburg coals of comparable feed size. A straight line has been fitted to this data.

$$\text{G.H.V.} = (221.1 - 29.8\ m_A/m_C)/m_C$$

At a fixed air rate, this equation predicts a maximum in the heating value with coal feed rate, and at fixed coal rate, a linear decrease in heating value with increasing air/coal ratio – the heating value characteristics illustrated in Figures 2 and 3. Within the scatter of the heating value data there appears to be no significant difference between fluidized- and spouted-bed operation, nor among three different shipments of Forestburg coal tested over the three-year period. Data points for smaller and larger coal particle sizes, not shown, appeared below and above the curve, respectively. The gas yield plot also shows no apparent difference between spouted-bed and fluidized-bed modes with coal shipment C. It appears that slightly lower yields were achieved with coal shipment B, and excluding this data a least squares fit yielded

$$\text{G.Y.} = m_C(0.062\ m_A/m_C - 0.077).$$

Thus the gas yield increases with the air/coal ratio at a constant coal feed rate, and at constant air rate decreases as the coal rate increases as shown in Figures 2 and 3. Plots similar to Figure 4 have been published for several coals (3).

The beneficial effects of coal of larger size are shown in Table 3. Gas calorific values showed a steady increase with particle size up to 3.5 mm. Because of the extensive work required to prepare narrow cuts such as $-4+8$, the remainder of the work has been done with $-4+18$ coal unless otherwise noted.

Recycle of product char from the primary cyclone has some beneficial effects on carbon conversion and efficiency factor as shown in Figure 5. While the heating value remains essentially constant, the gas yield per kg of feed coal increases, therefore improving the efficiency factor. The improvement of carbon conversion is slight, but significant.

The bed can either be operated with inert solids such as gravel or silica-sand, or be made up solely of the product char itself. With an active char bed, it is rather more difficult to control the gasifier given that at high gasification rates the bed may be consumed sufficiently fast enough that the bed level drops with time. A second potential disadvantage is that with the larger hold up of char, the generation of fines in the high-velocity inlet jet will increase and the elutriation of fine carbon dust will also increase. Balancing these drawbacks are the obvious advantages of simplicity of the system and the option to run in the ash-agglomerating mode.

There appears to be a minor effect on gas quality of operating in the char-bed mode, as is seen in Figure 6. Including some oxygen gasification data, Figure 7 shows the char-bed data to be essentially in agreement with the inert-bed data as far as efficiency factor is concerned, and a little higher in terms of carbon conversion (Fig. 8). Carbon conversions around 80% are achieved although this latter factor was not borne out for oxygen gasification of bituminous coal (see below).

Oxygen-Steam Gasification

With oxygen-steam gasification, a number of options exist. Runs can be done with air as the coal transport medium, thus giving a gas with nitrogen content below the 50-60% N_2 level of air gasification tests, but still containing some nitrogen. Figure 9 shows a rough correlation of the gas heating value with the nitrogen flow to the gasifier. A smooth relationship exists over the range of nitrogen inputs, and a heating value of about 9.8 MJ/m^3 is predicted at zero nitrogen input. The consistency of the oxygen gasification and air gasification data was already in evidence from Figure 7 in which the predicted efficiency factor correlation of the air tests is shown to predict values reasonably well for the subsequent tests of oxygen gasification.

In oxygen gasification control of bed temperature is possible by use of steam, to a degree not possible in air gasification. As the steam flow rate is decreased and bed temperature rises, the heating value of the gas improves (Fig. 10), and the carbon conversion increases (Fig. 11). This latter figure suggests for bituminous coal that operation in an inert bed gives better carbon conversion. Note that with bituminous coal the carbon conversion is lower than for subbituminous coal. This arises primarily because of decrepitation of the bituminous coal, and carry over of carbonaceous solids out of the bed. For these coals good gas cleaning and char recycle are essential for efficient operation.

The steam/oxygen level in the blast has a distinct effect on the H_2/CO ratio in the product gas from subbituminous coal. Figure 12 shows the effect of the blast composition on the H_2/CO ratio produced. It is evident that production of H_2/CO with ratios around 2, as required for synthesis of methanol for example, requires a blast of about 3 kg steam/kg oxygen with Forestburg coal, whereas to reach a H_2/CO molar ratio of 3, as required for synthetic natural gas, the steam/oxygen mass ratio must reach 3.6. For bituminous coal the molar ratio of H_2/CO is virtually unity for all H_2O/O_2 ratios in the blast, in sharp contrast to that of the subbituminous coal.

Agglomerating Ash Runs

Operation in the ash agglomeration mode requires a temperature in the agglomerating zone sufficiently high to render the ash particles sticky, but not so high as to produce slagging, which could result in a single large lump. In order to remove agglomerated material of a controlled size from the bed, the zone of agglomeration must be properly located, and provision made for the agglomerates to exit the reactor. In the present case agglomeration was induced by use of oxygen to produce a local high-temperature zone. A series of evolutionary changes were made to the flow piping and flow rates in the conical bottom of the reactor in order to achieve agglomeration. In the most successful of these runs, spherical agglomerates of about 5 mm containing less than 1% carbon were produced from Balmer coal (Fig. 13). These agglomerates were collected from the bottom of the cone. The temperature in the agglomerating region was about 1150°C. Continuous outflow of ash agglomerate will require modification to the cone section of the reactor and has not been demonstrated.

Catalytic Gasification Runs

The aim of these preliminary tests was to see if potassium, a known catalyst, applied as potassium carbonate, would be effective in improving carbon conversion or efficiency at a given temperature. Potassium carbonate solutions were sprayed onto the coal which was then dried at 30°C. Adhesion of the potassium-treated coal made necessary a further crushing step to break these agglomerates. Thus the particle size as fed was markedly different from that of the original coal. The original coal was typically 1.6-mm mean particle diameter whereas the 21.9% K_2CO_3 loaded coal used in Runs 110 and 111 averaged 0.6 mm in mean particle diameter. The less highly loaded coal of Run 109, at 12.1% K_2CO_3 was 1.3 mm in size. It has been established previously (Table 3) that smaller coal size leads to poorer performance. Results for the three runs are plotted in the earlier plots with other Balmer coal data. In Figures 11a and 11b it is clear that Run 109 is higher in carbon conversion and efficiency factor by about 15%-20% for the catalytic run at the same average bed temperature. At the higher potassium carbonate loading of ~21.9%, Run 110 shows the penalty paid by the reduced particle size, as the carbon conversion and efficiency are roughly that expected for the untreated coal. Because of the large carbon carryover for such small feed sizes, it is essential to recycle char from the cyclone. Data for Run 111 where this is done show the carbon conversion and efficiency gains are restored to levels comparable to those of Run 109, in spite of the 0.6 mm average feed size.

There is a price to be paid, then, for the presence of the K_2CO_3 on the coal, in that to feed the coal easily, some extra agglomerate crushing is required. The hygroscopic nature of the salt also causes problems at the feed point, where plugging is apt to occur due to the re-agglomeration or pick-up of steam by the carbonate on the coal surface. All three catalyst runs were bothered by feeding problems.

A further advantage of the presence of K_2CO_3 lies in the sulphur content of the produced gases. Table 4 shows no detectable sulphurous species in the gas for the catalytic runs in contrast to the 240-380 ppmv present in non-catalysed runs. Sulphur capture may well occur as the K_2CO_3 decomposes to K_2O which would react rapidly with the H_2S in the gas, yielding potassium sulphide. These few tests on catalytic gasification thus show a combination of advantages and disadvantages to the application of K_2CO_3.

In-Bed Gas Composition and Temperature Profiles

A set of gas sampling probes and a sampling train were constructed (Figure 14) and a number of ports drilled through the gasifier lining. During a series of runs, samples were taken at sampling velocities based on an approach to isokinetic sampling using velocity profiles calculated from equations available in the literature. Three radial locations each with six axial positions were used.

Typical profiles in air gasification of Forestburg coal are shown in Figure 15. Near the wall (Position A), in the gasifier annulus, the oxygen concentration is seen to drop to zero about 0.1 m above the inlet orifice. H_2 and CO concentrations rise smoothly and rapidly to values of about 24% near the top of the bed. The local CO_2 concentration goes through a minimum at the top of the conical section. At Position B, midway through the annulus, a similar oxygen profile is set up. A somewhat different profile exists for H_2 and CO with a point of inflection near the top of the conical section of the column. The relatively flat CO_2 profile matches that of oxygen. Near the centre of the column and in the spout region, the oxygen concentration persists to about 0.35 m of height rather than dropping to zero near the orifice as in the annulus. The CO_2 profile is the mirror image of the oxygen profile. H_2 and CO show no significant presence until the oxygen has dropped to about 2%, 0.35 m from the orifice. In general these profiles show that for air gasification, the oxidizing zone is in the spout region only and exists only near the bottom part of the reactor, the CO_2 patterns are complex (reflecting oxidation in the spout and perhaps pyrolysis in the annulus), and the H_2 and CO concentrations within the bed are everywhere in a molar ratio close to unity. Gas composition profiles were not changed markedly either by char recycling or by changes in bed depth, except that above the bed the H_2 and CO dropped off due to mixing of spout and annulus gas.

For the case of oxygen rather than air gasification of Forestburg coal, different types of profiles were observed (Fig. 16). At position A, 3.9 cm from the wall, the H_2 concentration is about twice the CO value and both level off within about 0.1 m of the orifice. At position B, the H_2/CO ratio is also about 2, and again flat until heights above the bed. In position C, which should be near the center of the spout, the oxygen concentration persists at a level of about 3% all along the spout. The CO_2 level here is extremely high at about 40%, and the H_2/CO ratio remains at about 2.

Plots of annulus profiles only are shown for Balmer coal (Fig. 17). These are basically similar to those observed with Forestburg, except that the H_2/CO ratio is lower. Thus the oxygen/steam gasification profiles show that H_2/CO levels are about 2 everywhere and higher than in the case of air gasification because of the higher H_2O/O_2 ratio. In addition, the profiles tend to be flatter than for air gasification and the CO_2 decreases smoothly with increasing bed depth above 0.2 m. Above the bed there is a drop in both H_2 and CO and a rise in CO_2 presumably due to gas phase combustion, mixing and reaction in the fountain region.

Temperature profiles are shown in Figures 18 and 19. For air gasification of Forestburg coal, there exists a large variation in the gas temperature along the spout referred to here as position C. The rapid rise from 700°C at the bed level $Z = 25$ cm to about 800°C at the bed level $Z = 35$ cm, is due to combustion, as is evident by the rapid drop in the oxygen concentration within the same bed levels shown in Figure 15. It is the combination of combustion and low incoming gas and solid temperature that results in a very large temperature difference in the spout. The temperature profile along position B, which is close to the annulus centre, is similar to that observed in a moving-bed gasifier. In this case the combustion reaction is responsible for the high-temperature at the bottom, while the drop in temperature towards the top is due to gasification reactions. The temperature profile along position A increases steadily to a maximum value in the lower half of the column and reduces thereafter. This low temperature at the bottom is the result of the endothermic C-H_2O and C-CO_2 reactions. The slight increase in values observed may have been due to the inflow of heat from the neighbouring region which is partly shown by the simultaneous decrease in temperatures along position B. In addition to the axial variation in gas temperatures there is also a significant radial temperature gradient, not only between the spout and the annulus, but also within the annulus itself, especially in the lower section of the bed.

The average temperature profiles for oxygen gasification of Forestburg coal (Run 94) along positions A, B and C are plotted in Figure 19. As in the previous case the rapid increase in temperature along the spout is due to the heat released from combustion. According to the composition profiles, there is still a substantial amount of oxygen along the centre of the column in the fountain. Hence combustion must also be responsible for the sharp increase in the gas temperature observed along this region.

Both the temperature profiles along positions A and B show similar trends increasing throughout the bed as well as in the fountain. The steady increase in temperature in the fountain is the result of gas mixing within the region to give a higher average gas temperature than that in the annulus. A very shallow bed was employed in this run. Thus it is possible that the continuous increase in temperature along the bed in the annulus is due to the higher temperature of the incoming solids from the fountain rather than combustion. Judging from the oxygen concentration along positions A and B as shown typically in Figure 16, it is unlikely that any combustion takes place in the upper section of the bed.

OVERVIEW OF RESULTS

This research program has shown that the spouted-bed gasifier is a very versatile reactor which can operate in a number of modes to produce gases of comparable quality to other designs which have evolved over many years.

Table 5 shows that the spouted-bed pilot unit generally compares well with other established units. Being a small-scale reactor with larger heat losses, and hence higher CO_2 levels in the off-gas, its gas-heating values and efficiency are slightly lower. Typical H_2/CO molar ratios are about 1.05-1.25 for bituminous coals, which are between values of 0.6 for the Westinghouse fluidized bed and the 2.2 of the Lurgi pressurized moving bed.

Carbon conversion can undoubtedly be improved upon scale-up with a larger free-board section and quantitative recycling of fines from the primary cyclones, although it will eventually be limited to values similar to those in any non-slagging system.

CONCLUSION

In this paper the influence of the major factors on the spouted-bed gasifier performance has been illustrated using tests on a series of coals. It has been shown that the spouted bed can be operated with a char or an inert bed, with air or oxygen in the blast, with dry or agglomerating ash, and with a catalyst. Bituminous and subbituminous coals have been treated. Profiles from within the gasifier outline the regions of combustion and gasification, and permit a reasonable approach to mathematical modelling of the reaction system.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the support of CANMET and recognize the contributions of S.K. Foong and C.B. Prakash to the experimental work, and of the CANMET Scientific Authorities, G. Sirianni, K. Thambimuthu, C.B. Prakash, and D. Fung.

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NOMENCLATURE

C.H.V.	Coal higher heating value	MJ/kg MAF coal
G.H.V.	Gas higher heating value	MJ/m^3 gas at S.T.P.
G.Y.	Gas yield	m^3 gas at S.T.P./kg MAF coal
H	Average bed height	(m)
M_a	Air rate	kg/s
M_C	Coal rate	kg MAF coal/s
M_{Ch}	Coal recycle rate	kg MAF char/s
M_{O2}	Oxygen rate	kg oxygen/s
$\bar{T}_b$	Mean bed temperature	°C
Z	Distance above orifice	(m)

TABLES

Table 1 – Operating modes of spouted-bed gasifier

Inert Bed	versus	Char bed
Air Blast		Oxygen blast
Char recycle		Single Pass
Dry Ash		Agglomerating Ash
Non-catalytic		Catalytic Gasification
Clean coal		Reject Coal (~50% Ash)
Subbituminous Coal		Bituminous Coal
Caking Coal		Non-caking Coal

Table 2 – Coals treated in the spouted-bed gasifier

Coal	Rank	% Moisture	% Volatiles	% Fixed Carbon	% Ash	F.S.I.
Forestburg	Subbit	23.7	29.4	33.5	13.6	1
Roselyn	Subbit	27.0	29.1	39.9	4.0	1
Klimax	Lignite	35.9	25.2	33.7	8.1	1
Coleman	Bit	3.	24.5	62.7	9.8	3.5
Sukunka	Bit	1.1	20.6	65.1	13.3	7
Balmer	Bit	1.5	20.1	67.0	11.5	1.5
Balmer Reject	Bit	1.6	15.4	28.3	55.6	1.5

Table 3 – Effect of particle size in air gasification*

Coal Size Range Sieve No.	Average Size (mm)	Bed Carbon Content (% wt)	Gas Heating Value MJ/m³
−18 +45	0.74	<1	2.84
80% −6 +18 20% −18 +0	1.39	15	3.47
−6 +18	2.06	45	4.36
−4 +8	3.54	26	4.41

* *Forestburg coal*

Table 4 – Sulphur levels in gases from Balmer coal

Run No.	Mode of gasification	Conc'n in gas (ppmv) H_2S	SO_2	Per cent of S in gas (wt %)
107	ash agglomeration	240	2.7	30.2
108	ash agglomeration	343	3.6	41.4
109	catalytic	33	—	
110	catalytic	Not detected		
111	catalytic	Not detected		
112	ash agglomeration	378	0.9	

Table 5 – Comparison of oxygen-fired gasifiers

Gasifier	Winkler	KT	Texaco	Lurgi	Westinghouse PDU	Spouted-Bed Pilot	
Gasifier type	Fluidized Dry Ash	Entrained Slagging	Entrained Slagging	Moving Dry Ash	Fluidized Agglo-Ash	Dry Ash	
Coal	Lignite	Bit.	Bit.	Bit.	Bit.	Forestburg(85)	Balmer(82)
Pressure (MPa)	0.1	0.13	4.0	2.5	1.08	0.1	0.1
Temp. (°C)	980	1925	1400	980-1370		903	932
Steam/Oxygen (kg/kg)	0.5	0.4	0.5	4.0	1.0	3.0	3.4
Gas Composition (mole %)							
CO	48	53	52	18	49.1*	26.3**	29.6**
CO_2	14	10	12	30	17.2	34.5	30.6
H_2	35	36	35	40	29.8	36.0	36.2
CH_4	2	—	—	9	3.2	3.2	3.03
N_2	1	—	—	1	0.3	—	—
Others	—	—		2	—	—	—
Gas Calorific Value (MJ/m³)	10.7	11.3	11.1	11.3	10.7	8.7	9.1
Cold Gas Efficiency (%)	72	75	75	80		76	65

* *Purge free bases*

** *N_2 – free basis*

References: *Probstein and Hicks "Synthetic Fuels"*
McGraw-Hill (1982)
Salvador et al: "The Westinghouse Coal Gasification Process", Int's Gas Res. Conf., June 1980.

FIGURES

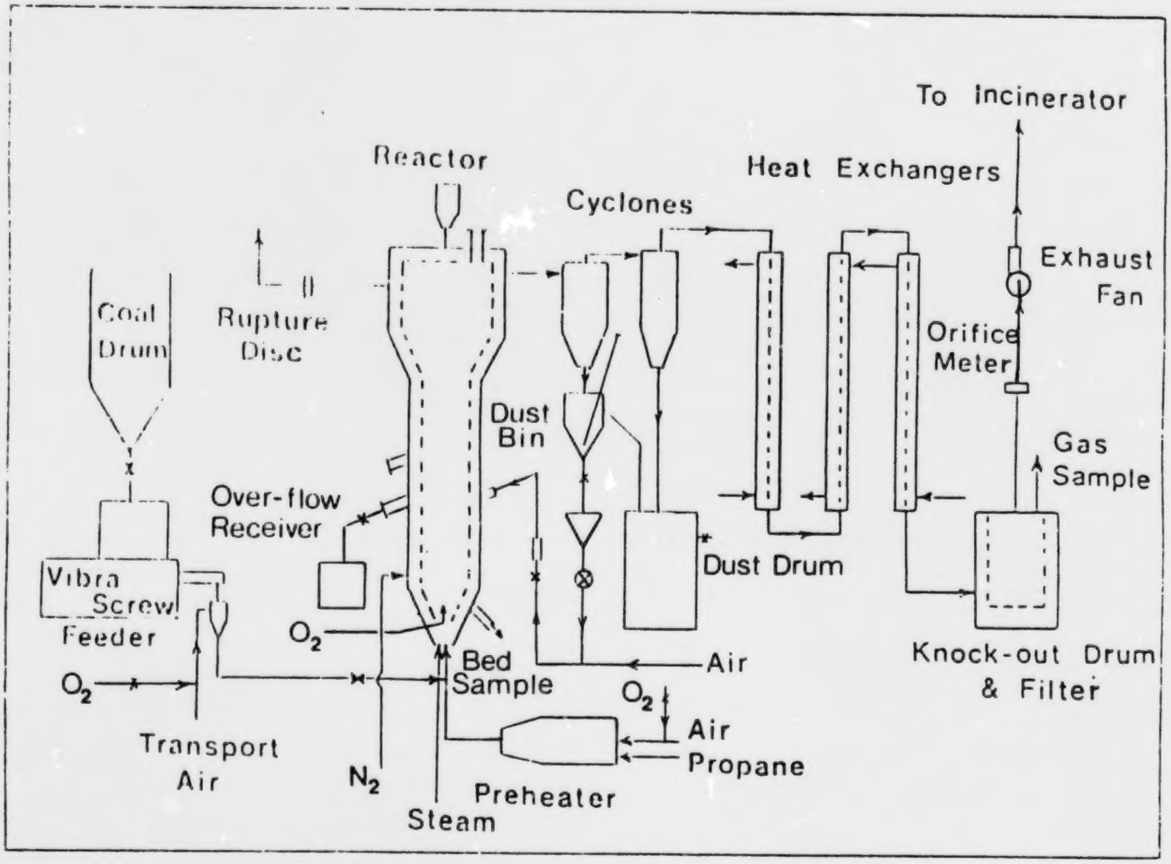

To Incinerator
Reactor
Heat Exchangers
Cyclones
Exhaust Fan
Coal Drum
Rupture Disc
Orifice Meter
Dust Bin
Gas Sample
Over-flow Receiver
Dust Drum
Vibra Screw Feeder
O_2
Bed Sample
Air
Knock-out Drum & Filter
O_2
O_2
Air
Transport Air
Propane
N_2
Preheater
Steam

Fig. 1 – Flow diagram of the process development unit

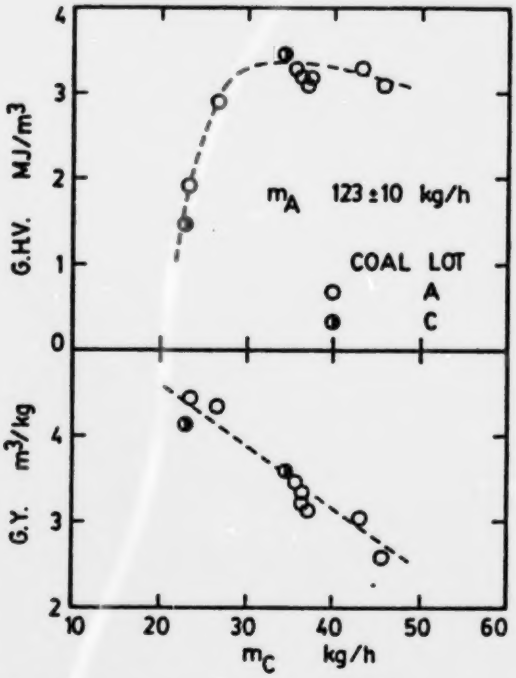


Fig. 2 – Effect of coal feed rate (M.A.F. basis) at a constant air rate on gas heating value and gas yield for Sukunka coal in a spouted bed. (Coal shipment A = 1979-80, C = 1981-82)

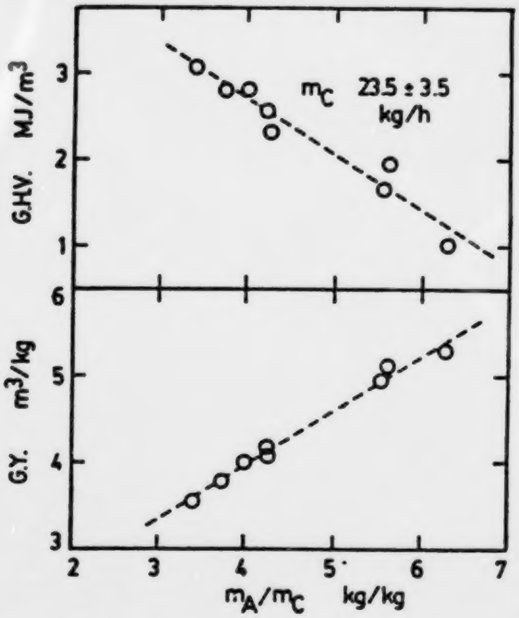


Fig. 3 – Effect of air/coal mass ratio (M.A.F. basis) at a constant coal rate on gas heating value and gas yield for Roselyn coal in a spouted bed.

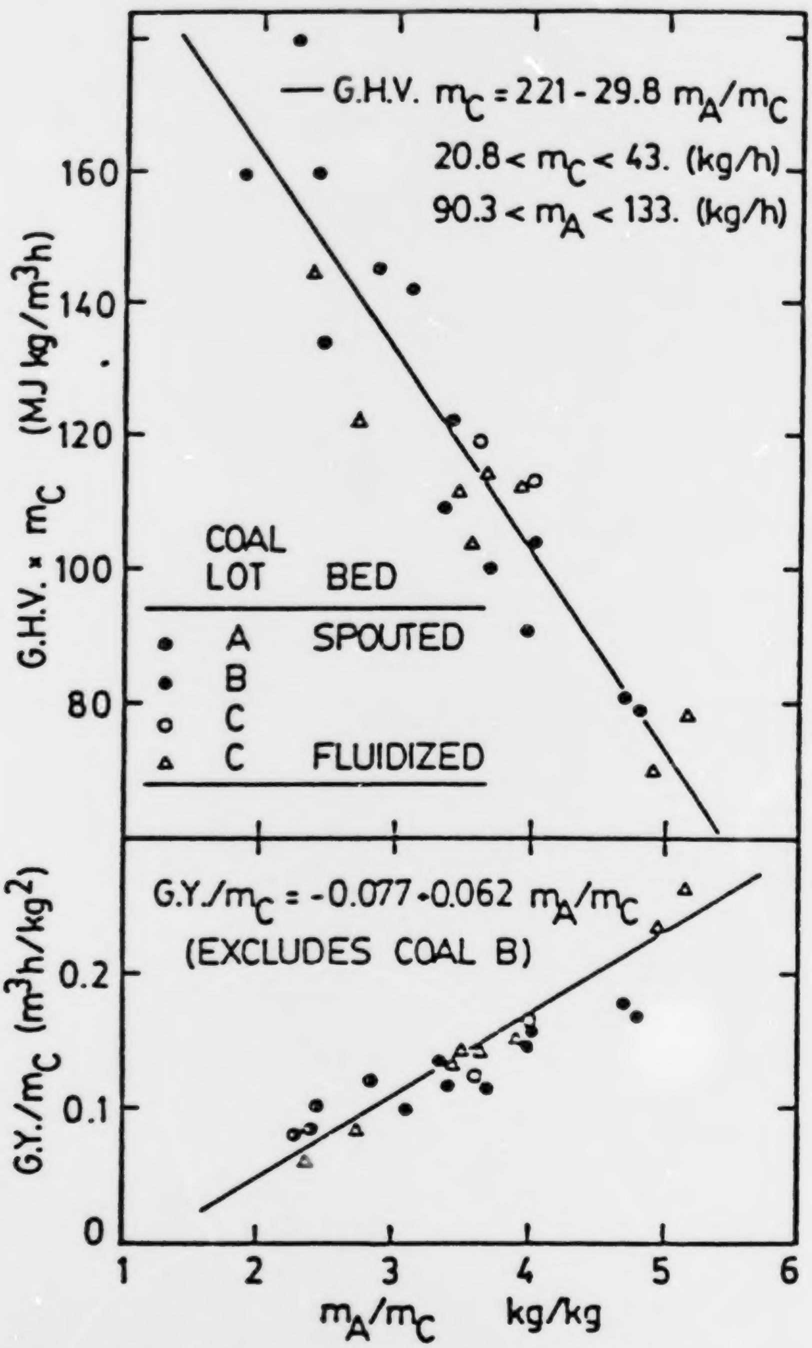


Fig. 4 – Gas heating value and yield functions versus air/coal ratio for Forestburg coal in spouted and fluidized beds (A = 1979-80, B = 1980-81, C = 1981-82 coal shipments)

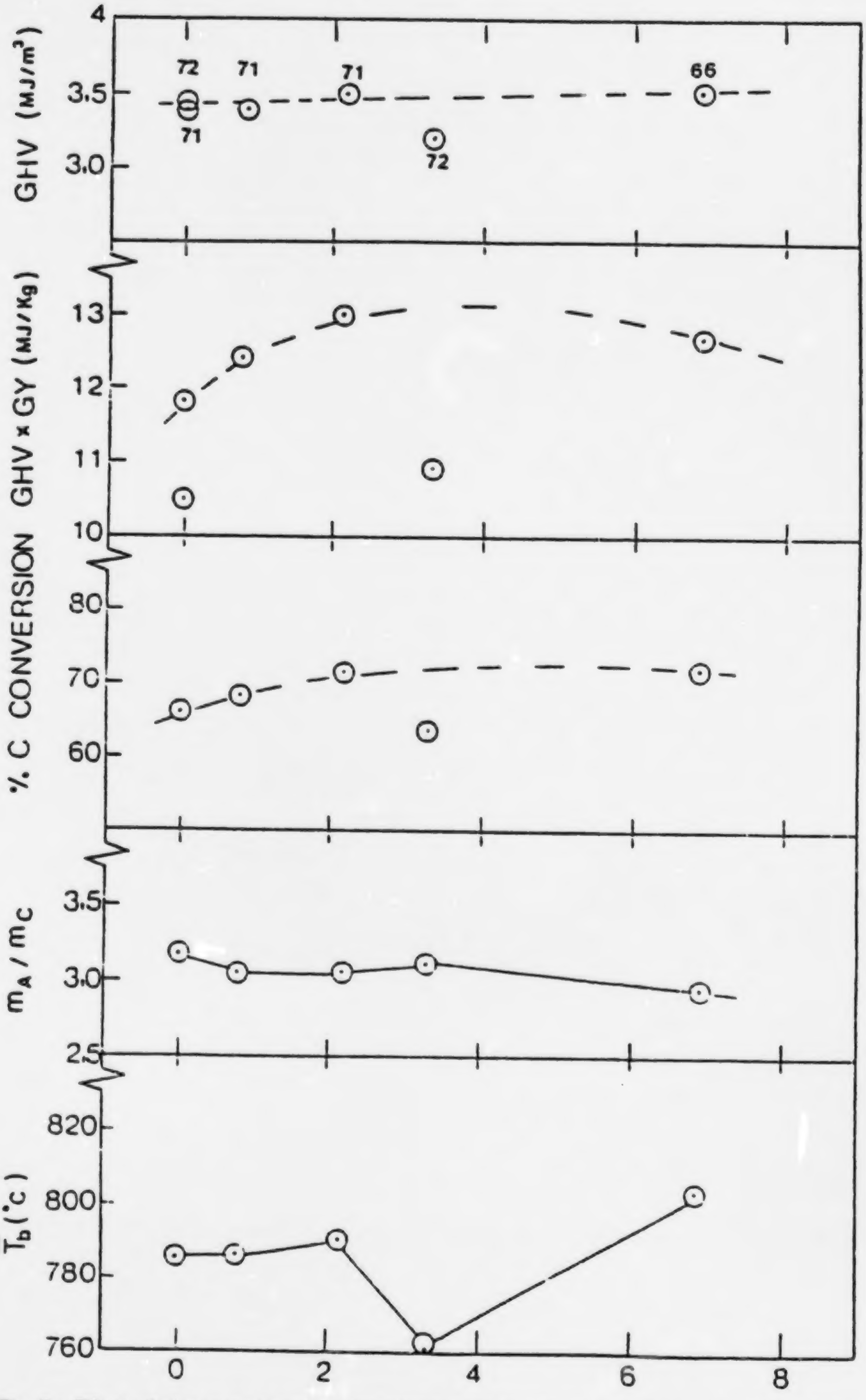


Fig. 5 – Effect of char recycle rate – Forestburg coal (numbers refer to experimental runs)

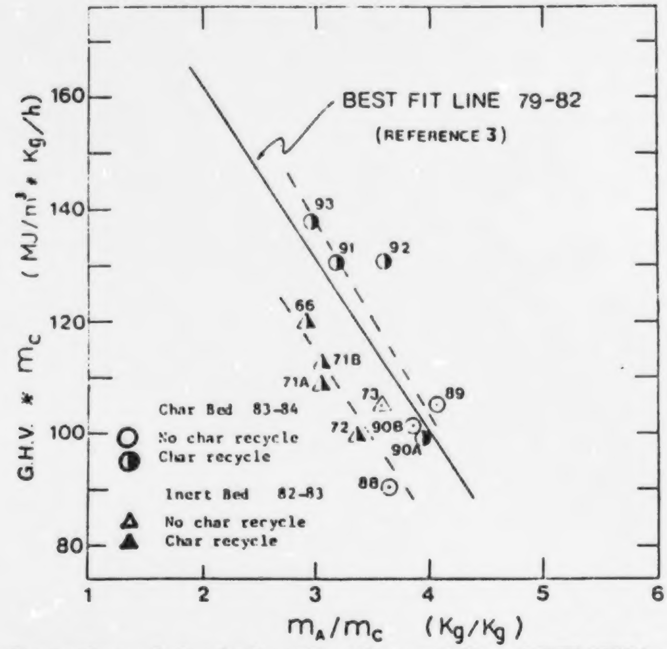


Fig. 6 – Comparison of char bed results with correlation of 1979-1982 inert bed data

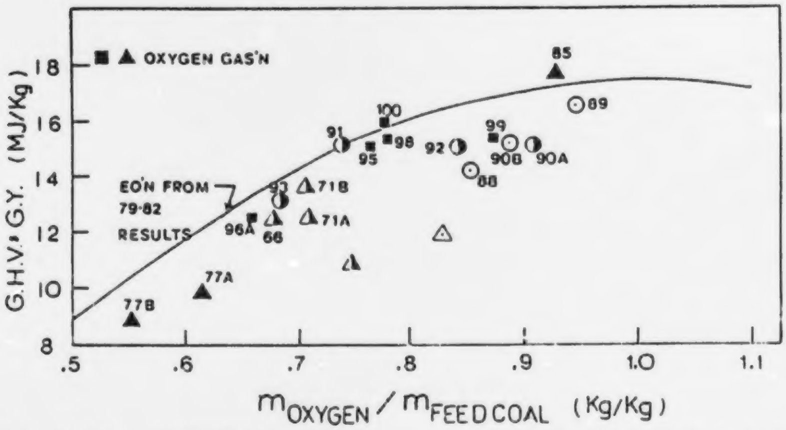


Fig. 7 – Comparison of efficiency function for char bed runs with inert bed run equation from 1979-1982. Results for Forestburg coal (see Fig. 6 for legend).

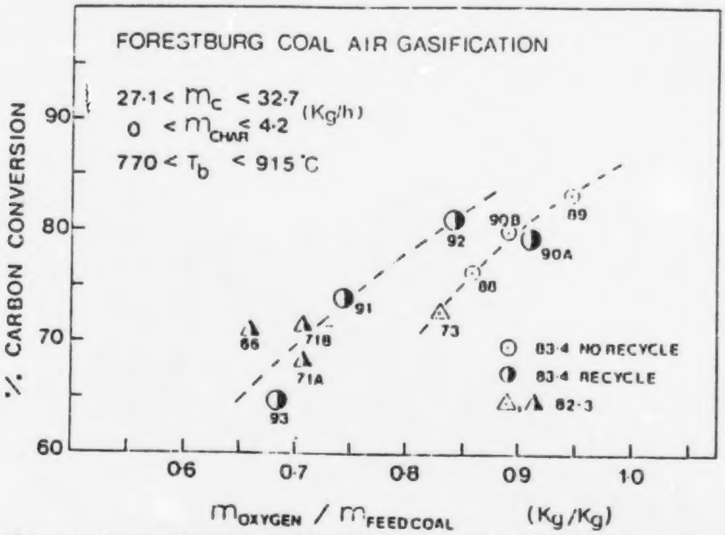


Fig. 8 – Effect of oxygen/coal ratio on overall carbon conversion (Forestburg coal – air gasification).

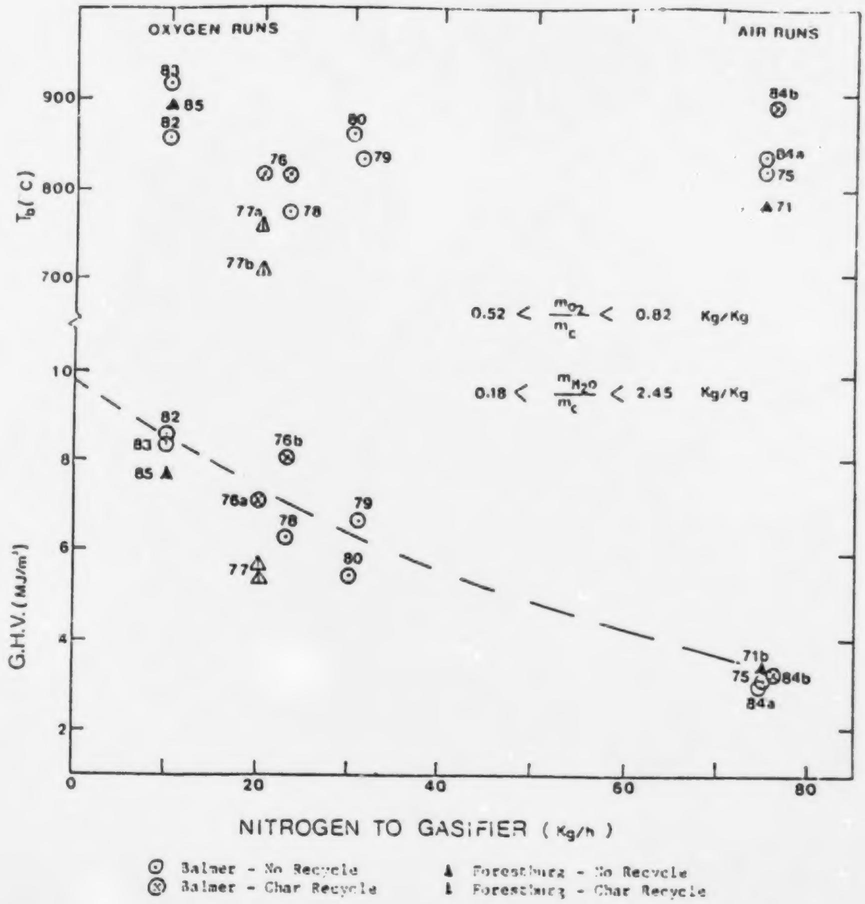


Fig. 9 – Effect of nitrogen flowrate on gas heating value and bed temperature

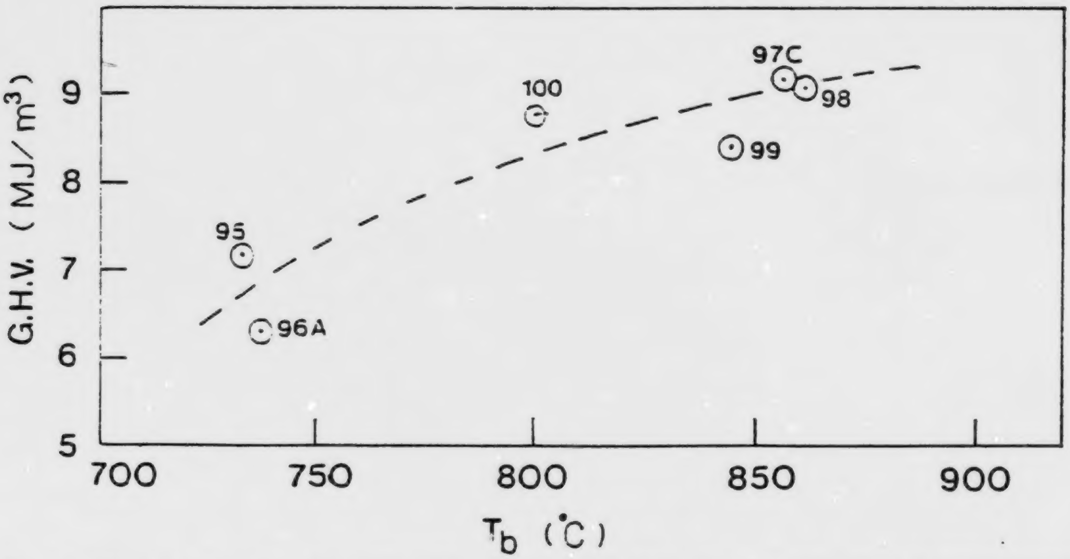


Fig. 10 – Effect of average bed temperature on gas heating value for oxygen gasification of Forestburg coal

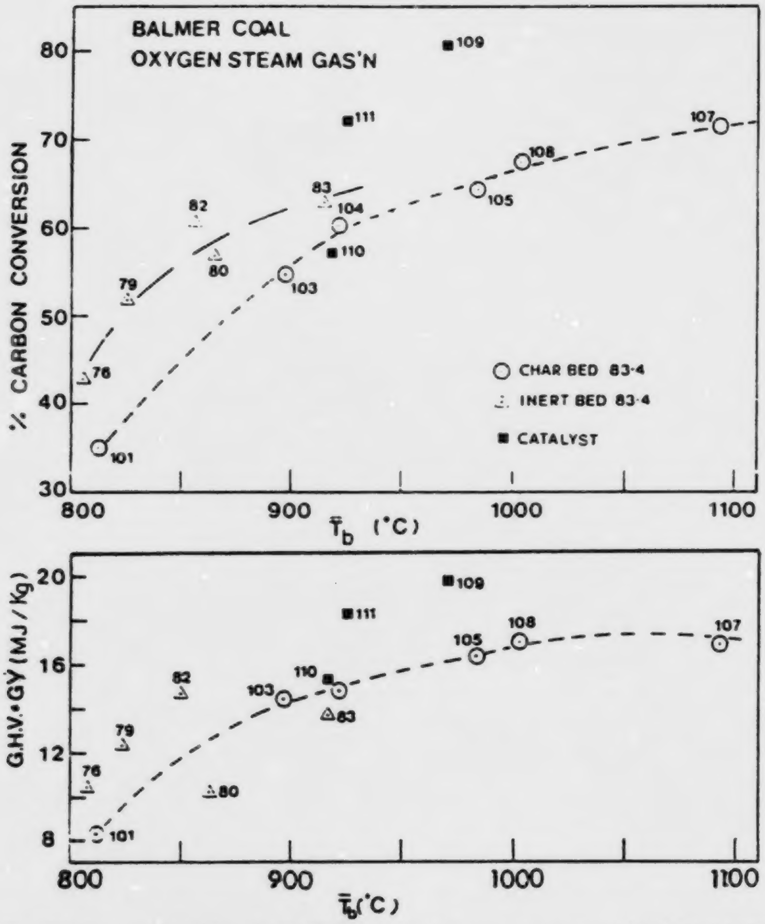


Fig. 11 – Carbon conversion and efficiency factor versus average bed temperature

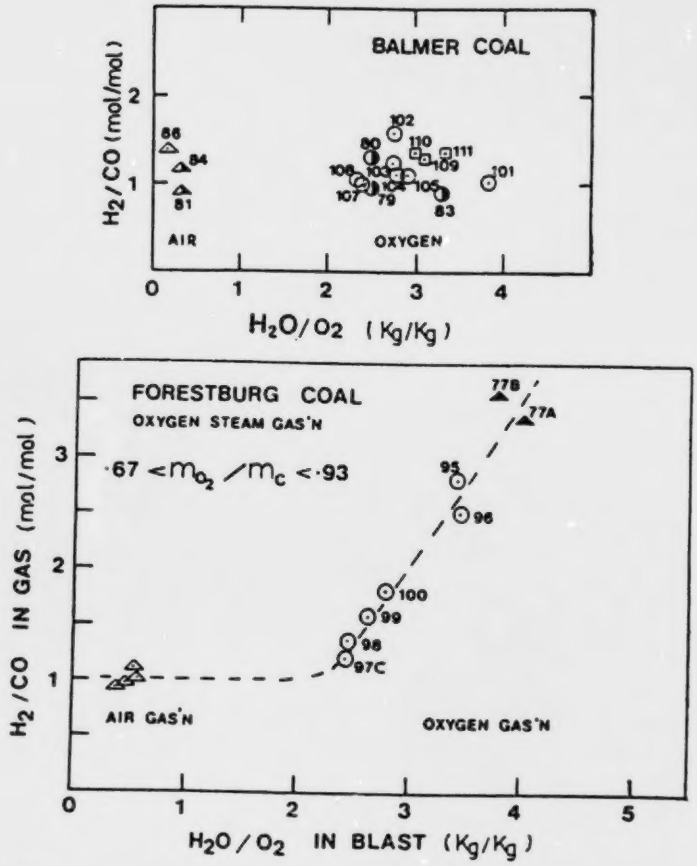


Fig. 12 – Effect of steam/oxygen ratio in blast on H_2/CO ratio in gas

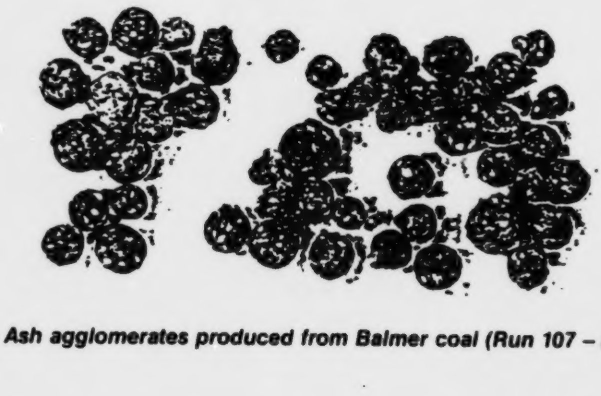
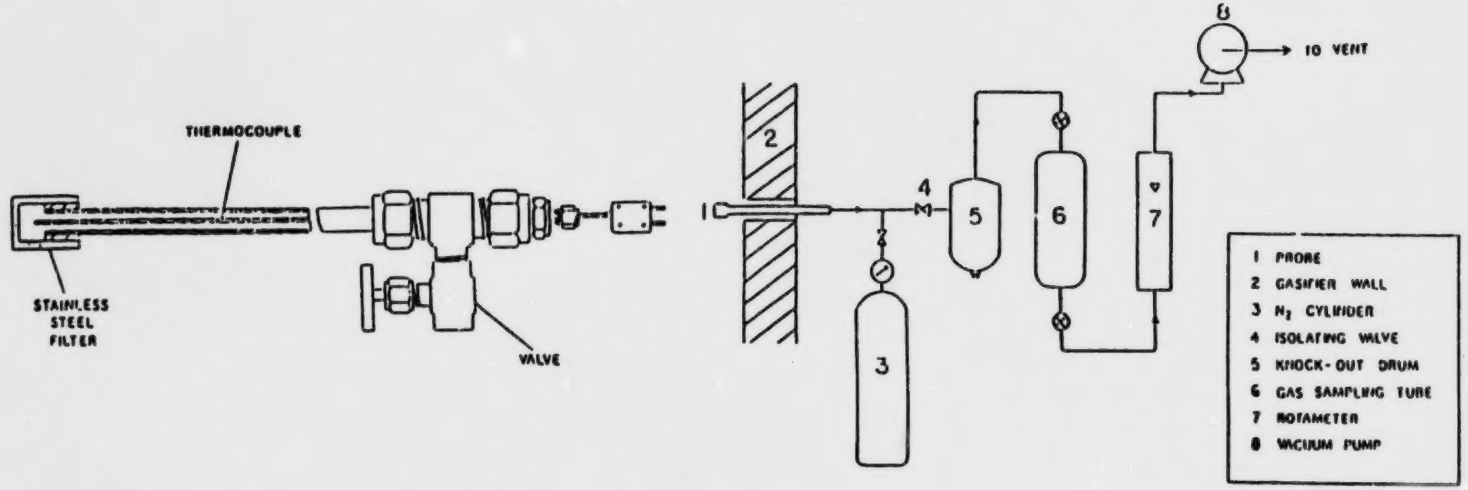


Fig. 13 – Ash agglomerates produced from Balmer coal (Run 107 – actual size)


THERMOCOUPLE
STAINLESS STEEL FILTER
VALVE
1
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TO VENT
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2 GASIFIER WALL
3 N_2 CYLINDER
4 ISOLATING VALVE
5 KNOCK-OUT DRUM
6 GAS SAMPLING TUBE
7 ROTAMETER
8 VACUUM PUMP

Fig. 14 – Gas sampling probe and flow diagram

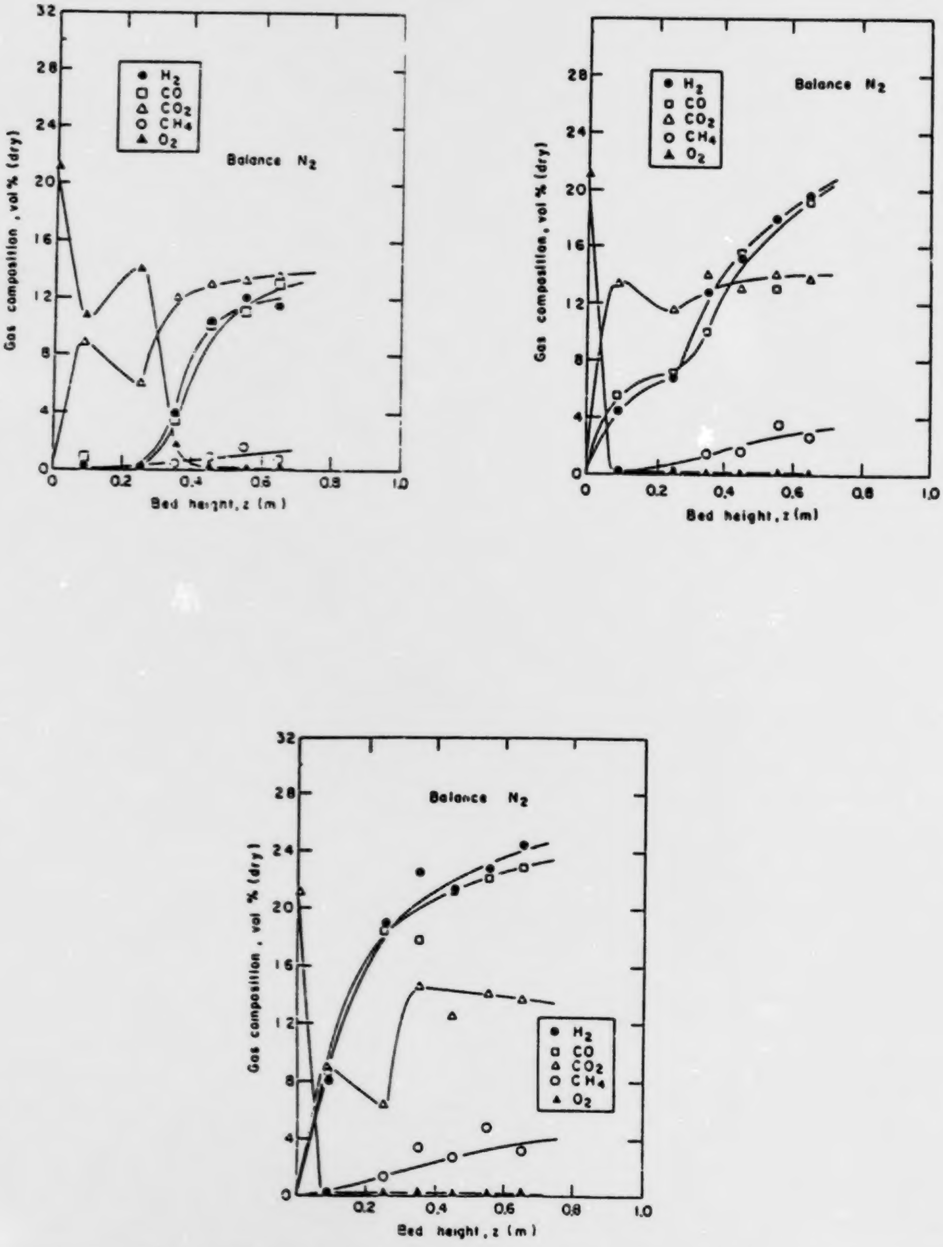

Fig. 15 – Ash gas composition profiles along positions A, B and C for Forestburg coal – air gasification (Run 93).

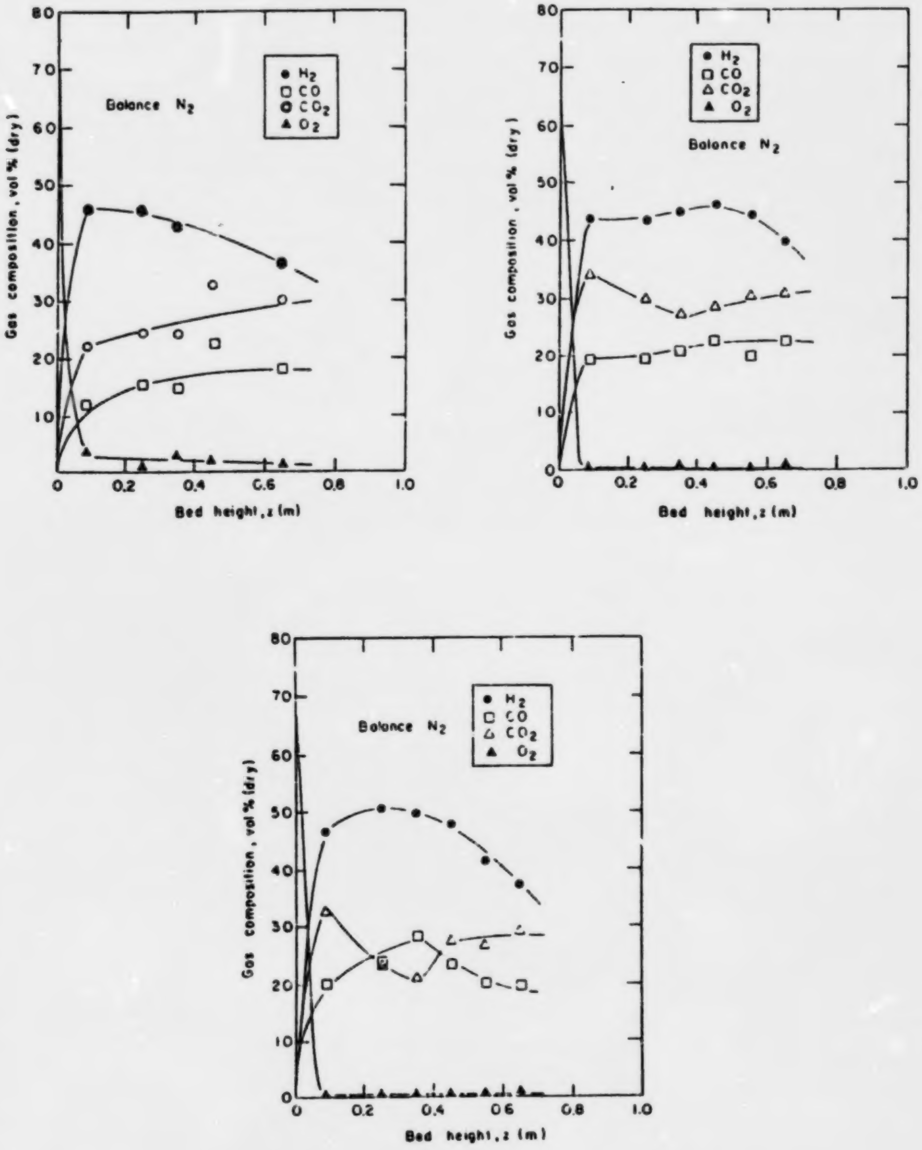

Fig. 16 – Axial gas composition profiles along positions A, B and C for Forestburg Coal – oxygen (Run 96)

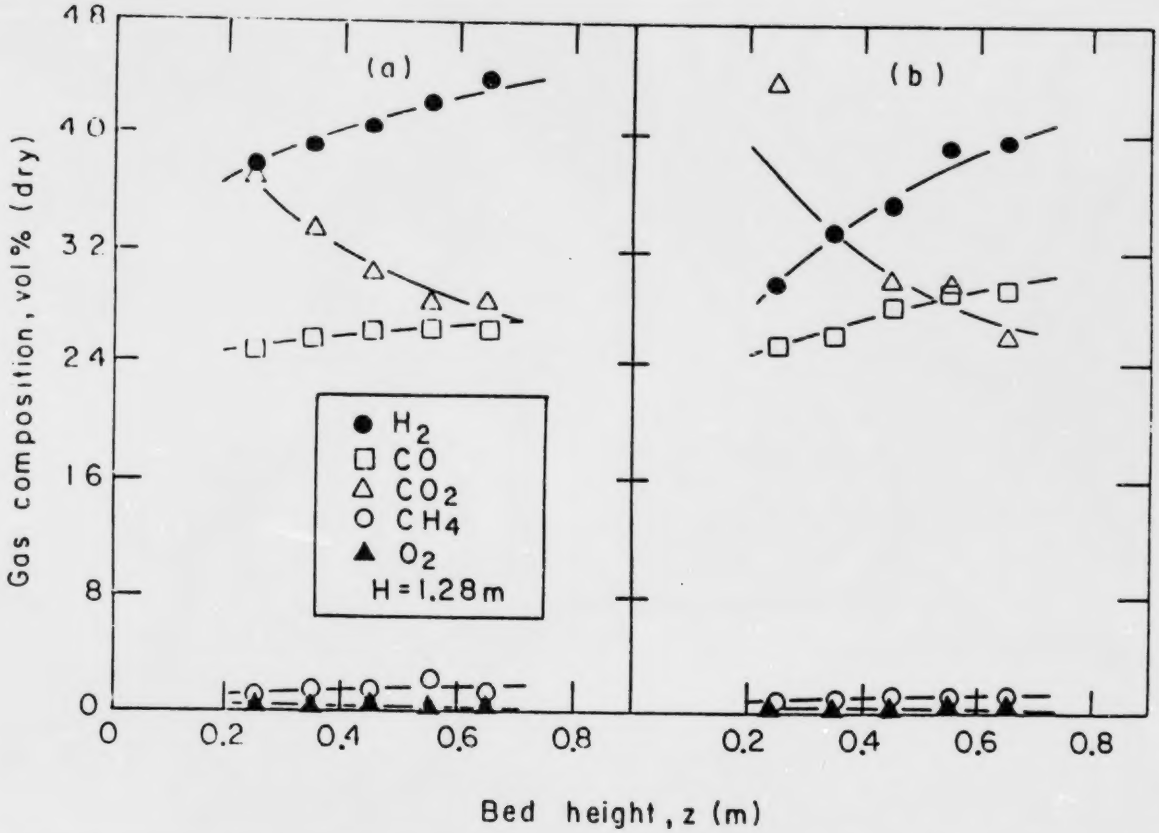

Fig. 17 – Axial gas composition profiles for Balmer coal-oxygen system in Run 103: a) Along position A, b) Along position B

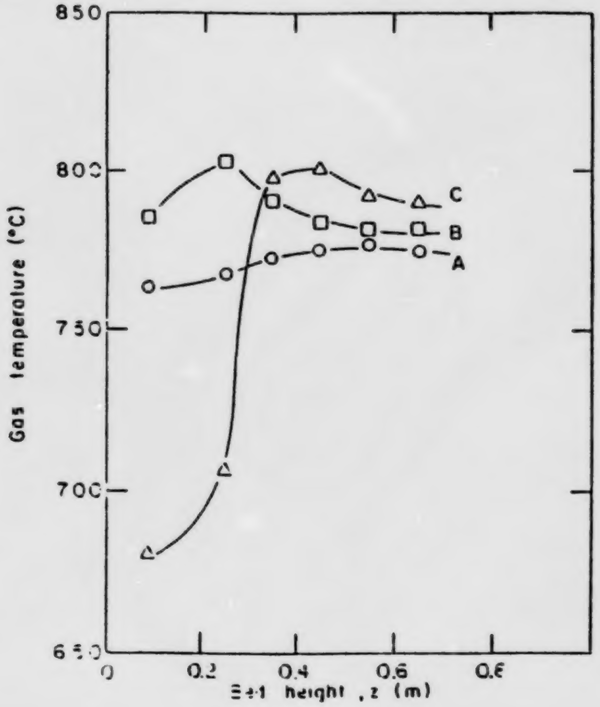

Fig. 18 – Axial temperature profiles for Forestburg coal – air system (Run 93) at positions A, B and C

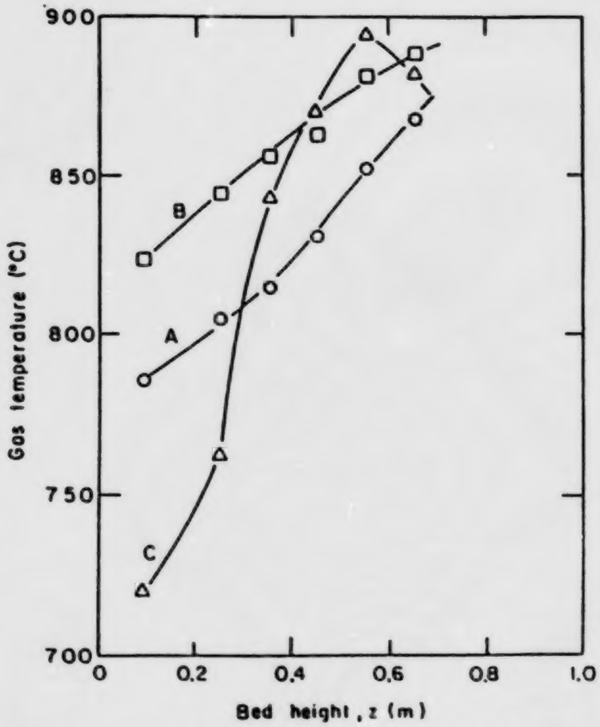

Fig. 19 – Axial temperature profiles for Forestburg coal – oxygen (Run 94) at positions A, B and C.

SESSION IV: PAPER 16

INDIRECT LIQUEFACTION OF ONTARIO LIGNITE

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ABSTRACT

Conversion of lignite to methanol or liquid transportation fuels using advanced lignite gasification/synthesis gas conversion technologies offers one of the best prospects for increasing domestic energy output within the next decade. With substantial reserves of lignite in Ontario, conversion to methanol or conventional liquid transportation fuels is of particular interest.

Kilborn was selected by Ontario Energy Corporation in February 1983 to evaluate the feasibility of converting Ontario lignite into methanol. Four commercial or near commercial gasification technologies were evaluated, and the most technically acceptable and economically attractive process was selected for testing. Test data were used to develop preliminary cost information on the production of methanol from lignite.

The test data confirmed that Ontario lignite can be efficiently gasified via the High-Temperature Winkler fluidized-bed gasification process. Production cost for the methanol, at a capital recovery factor of 20%, was estimated to be in the order of $290-370/tonne (23-26 cents/litre), depending on the downstream process used.

**denotes speaker*

PRÉSENTATION 16

LA LIQUÉFACTION INDIRECTE DU LIGNITE DE L'ONTARIO

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Toronto (Ontario) Canada

RÉSUMÉ

La conversion du lignite en méthanol ou en carburants liquides en faisant appel aux technologies avancées de gazéification du lignite et de conversion du gaz de synthèse, offre l'une des meilleures perspectives pour améliorer la production énergétique intérieure durant la prochaine décennie. Comme l'Ontario possède d'importantes réserves de lignite, la conversion du lignite en méthanol ou en carburant liquide pour les transports classiques présente un intérêt particulier.

La société Kilborn a été choisie par la Société d'énergie de l'Ontario en février 1983 pour évaluer la possibilité de transformer le lignite ontarien en méthanol. Quatre technologies de gazéification, commerciales ou près de l'être, ont été évaluées et le procédé le plus acceptable sur le plan technique et le plus attrayant sur le plan économique a été retenu à des fins d'essai. Les données fournies par ces essais ont servi à établir des renseignements préliminaires sur les coûts de production du méthanol tiré du lignite.

Les données des essais ont confirmé que le lignite ontarien peut être transformé efficacement en gaz en utilisant le procédé Winkler de gazéification des fluides à haute température. On a estimé que le coût de production du méthanol, en retenant un facteur de récupération du capital de 20 %, est de l'ordre de 290 $ à 320 $/tonne (de 23 à 26 cents/litre) selon le procédé utilisé.

**indique de conférencier*

INDIRECT LIQUEFACTION OF ONTARIO LIGNITE

INTRODUCTION

Lignite reserves in northern Ontario are estimated to be 92 million tonne. The lignite deposits are chiefly located in the area of Onakawana, northern Ontario, approximately mid-way between Smooth Rock Falls and Moosonee.

A potential use for this lignite is indirect liquefaction by gasification to produce a synthesis gas which can be converted to methanol via established technologies. The study, performed by Kilborn on behalf of Ontario Energy Corporation and CANMET, Energy, Mines and Resources, examined the technical and economic aspects of a number of gasification and downstream processing techniques.

The study was divided into four distinct phases:

Phase O: An assessment of four gasification process technologies in terms of their capabilities to indirectly liquefy Ontario Lignite to methanol and other liquid fuels.

Phase 1: Determination of the gasification/conversion process most economically attractive for the conversion of Ontario lignite to methanol and other liquid fuels. This included an evaluation of coprocessing options, natural gas/lignite or electrolytic hydrogen/lignite coprocessing, to produce a synthesis gas for conversion to methanol.

Phase 2: Testing of Ontario lignite at the process developer's facilities to confirm suitability of lignite as a feedstock for gasification and to provide process data to update the technical and financial information developed in Phase 1.

Phase 3: Preparation of an update of the Phase 1 process and financial data for the recommended gasification technology.

The data provided in Phase 3 was used by Ontario Energy Corporation in preparation of its report to the Ontario Ministry of Energy on the conversion of Ontario's indigenous resources of peat, lignite and wood to methanol and other liquid fuels by direct and indirect liquefaction methods.

PHASE O PROCESS ASSESSMENT

Four gasification processes were evaluated in Phase O. A prime stipulation was that the processes being considered must be commercially proven or at an advanced stage of development with commercialization being likely before 1990. The four technologies considered were:

1. Koppers-Totzek Entrained-Bed Process
2. Lurgi Fixed-Bed Process
3. Westinghouse Fluidized-Bed Process
4. High-Temperature Winkler Fluidized-Bed Process.

The Koppers-Totzek and Lurgi processes have been commercially proven using lignite as feedstock, while the Westinghouse and High-Temperature Winkler Processes are near-commercial with large pilot-plant (30-35 t/d) facilities in operation.

Each technology was reviewed with respect to its ability to gasify Ontario lignites, placing emphasis on the following parameters and considerations:

- Predicted behaviour of Ontario lignite in the gasifiers considering proximate, ultimate, ash and petrographic analyses of the lignite. Particular emphasis was placed on moisture content, ash content and ash fusion temperature characteristics of the Ontario Lignite.
- Expected synthesis gas composition and downstream processing requirements typical to each gasification process.
- Extent of commercial and/or pilot-plant experience, particularly with lignites displaying properties similar to Ontario lignites.

- Process and operating performance assessment with emphasis on the following aspects:
  - lignite preparation for efficient processing
  - expected yield, carbon conversion and thermal efficiency
  - start-up, shut-down and operating flexibility of the gasifiers
  - mechanical and materials performance.
- Environmental requirements in order to meet applicable federal and provincial guidelines.
- Contact with each technology developer to obtain his initial prediction of gasification potential based on the analysis of the Ontario lignite.

A summary of these key process characteristics is given in Table 1.

All four gasification technologies were recommended to be carried forward to Phase 1 for economic assessment. Each process was considered suitable for the gasification of Ontario lignites based on the technology review and predictions made by the developers. It was recommended that particular emphasis in Phase 1 be placed on the following aspects:

- Lignite predrying requirements and the possible effect on fines generation, particularly with respect to the Lurgi process. Lurgi (the process developer) indicated that, due to the high-moisture content of the Ontario lignites, severe decrepitation of lignite may occur during predrying, causing excessive fines' generation which cannot be handled efficiently in the gasifiers.
- Synthesis gas processing options to produce an optimum H_2/CO ratio for methanol synthesis.

PHASE 1 PROCESS EVALUATION

Phase 1 consisted of:

1. Preparation of a preliminary process design for each gasification technology for base case lignite only and coprocessing options.
2. Preparation of order of magnitude capital cost and operating cost estimates in first-quarter 1983 Canadian dollars for process plants located in Onakawana, Ontario. From the capital and operating cost data, product costs per tonne of methanol were developed for each technology.

A listing of the base cases and options considered is given in Table 2.

Figure 1 shows the downstream processing sequence of raw synthesis gas from the high-temperature gasifiers, Koppers-Totzek, Westinghouse and H.T. Winkler, in the base cases. The Westinghouse gasifier produces sufficient methane that a small steam methane reformer is justified to supplement the hydrogen for increasing the H_2/CO ratio to methanol synthesis.

Figure 2 shows the downstream processing requirements of the base case low-temperature Lurgi gasifier syngas. Significant quantities of methane, produced in the Lurgi process, are steam reformed. The Lurgi gasifier, because of the low-gasification temperature, also produces tars, tar oils, phenols and naphtha. These components are recovered in a relatively complex recovery system and combusted for steam generation. Although these compounds could be stored and marketed, the remote location of the complex and subsequent high transportation costs to markets precluded this option.

Of the four gasifiers considered in this evaluation, only Lurgi produced a satisfactory H_2CO ratio in the raw synthesis gas for methanol production. Synthesis gas from the Westinghouse, Koppers-Totzek and H.T. Winkler gasifiers must be shifted to increase the hydrogen content. Another method of increasing hydrogen content in the syngas is to add additional hydrogen from a natural gas source. For the above-mentioned gasifiers two optional process configurations were considered:

Option I: Steam reforming of natural gas to a hydrogen rich synthesis gas. This synthesis gas was blended with gasifier raw synthesis gas in appropriate proportions to obtain the desired H_2/CO ratio for methanol synthesis. See Figure 3.

Option 2: Steam-reformed natural gas is shifted to maximum hydrogen content and fed to a Pressure Swing Adsorption (PSA) unit. High-purity hydrogen from the PSA unit is blended with gasifier synthesis gas to obtain the desired H_2/CO ratio for methanol synthesis. See Figure 4.

An alternate method of increasing the hydrogen content in the synthesis gas of the Westinghouse, Koppers-Totzek and H.T. Winkler gasifiers is to add electrolytic hydrogen. For these gasifiers two additional process configurations were considered:

Option 3: Electrolysis of water to yield high-purity hydrogen and oxygen. Oxygen is sent to the gasifier while the hydrogen stream is blended with gasifier synthesis gas to obtain the desired H_2/CO ratio for methanol synthesis. Power for electrolysis is purchased. See Figure 5.

Option 4: Electrolysis of water similar to Option 3, but power is produced onsite by co-generation using lignite as fuel. This option was evaluated for the Westinghouse gasifier only.

In the Lurgi base case configuration, methane rich purge gas from the methanol synthesis unit is split and a portion steam reformed to a hydrogen rich synthesis gas for recycle to the methanol synthesis unit. An optional process configuration was considered for this gasifier:

Option A: A portion of the methanol synthesis purge gas is fed to a partial oxidation (POX) unit. Partial combustion of the purge gas with oxygen yields a hydrogen rich synthesis gas suitable for recycle to the methanol synthesis unit. See Figure 6.

The lignite analysis, presented in Table 3, was used as the basis for this phase of the study. It is the arithmetic average of the proximate and ultimate analyses of two samples, performed by CANMET. These analyses were also used by the Ontario Ministry of Energy in its Direct Liquefaction Study.

Order of magnitude cost estimates were prepared for the base case and options of an Onakawana lignite to methanol plant. Since the prime objective of Phase 1 was to compare the four technologies on a common basis, the following costs were not included:

- infrastructure costs such as townsite, roads, rail, etc.
- existing rail upgrading
- methanol distribution system costs
- mine development costs.

Costs of gasification and process plants were obtained from in-house Kilborn data and from communication with process developers and licensors.

Operating costs consist of the costs of raw materials, purchased utilities and services, labour, maintenance and overhead. Raw material costs were:

Lignite: $15/tonne as received, provided by Manalta Coal

Natural Gas: $.165/Nm^3 at the plant gate, provided by Northern & Central Gas

Power: $.0271/kWh, provided by Ontario Hydro.

Capital and operating cost summaries are provided in Tables 4, 5, 6 and 7 for the base cases, natural gas coprocessing options, electrolytic hydrogen options and the Lurgi partial oxidation option.

The thermal efficiencies of the processes for the base cases and options were determined, as follows:

		(Per cent)
Koppers-Totzek	Base Case	42.0
	Option 1	63.9
	Option 2	57.9
	Option 3	46.0
Lurgi	Base Case	53.3
	Option A	50.7
Westinghouse	Base Case	51.1
	Option 1	65.7
	Option 2	59.9
	Option 3	57.9
	Option 4	43.0

H.T. Winkler	Base Case	48.7
	Option 1	65.2
	Option 2	58.1
	Option 3	52.8

Overall Thermal Efficiency is defined as follows:

Base Case:

$$\frac{\text{(Methanol HHV)}}{\text{(Lignite to Gasifiers and Boiler.HHV)} + \text{Power}^*}$$

Options 1 & 2:

$$\frac{\text{(Methanol.HHV)}}{\text{(Lignite to Gasifiers \& Boiler.HHV)} + \text{(Natural Gas to Reformer Process and Fuel.HHV)} + \text{Power}^*}$$

Option 3:

$$\frac{\text{(Methanol.HHV)}}{\text{(Lignite to Gasifiers and Boiler.HHV)} + \text{Power}^*}$$

Option 4:

$$\frac{\text{(Methanol.HHV)}}{\text{(Lignite to Gasifiers \& Combined Cycle Power Generation System.HHV)}}$$

PHASE 1 CONCLUSIONS AND RECOMMENDATIONS

The main conclusions resulting from the Phase 1 study were:

1. The fluidized-bed technologies, Westinghouse and H.T. Winkler, consistently had the lowest cost for the base case and options.
2. The Lurgi process is not competitive due to excessive lignite fines' generation in the drying process. These fines cannot be processed in the Lurgi gasifier.
3. Koppers-Totzek process costs are high due to the extensive synthesis gas compression cost and the high steam generation requirement for steam turbine drivers.
4. The High-Temperature Winkler process is more likely to be commercialized than Westinghouse. A lignite-to-methanol plant operated by Rheinbraun is scheduled to start up in late 1984 in Berrenrath, West Germany. The Westinghouse technology received a temporary setback with the cancellation of its demonstration plant in Secunda, South Africa, but is currently being offered commercially by Kellogg Rust Westinghouse Energy Systems Inc.

The prime recommendations of the Phase 1 study were that:

- A test program be pursued with Rheinbraun Consulting GmbH using the High-Temperature Winkler gasification process.
- The process and cost data be updated to reflect the process developers' predictions as a result of the test program.

PHASE 2 TEST PROGRAM

Two drums of Onakawana lignite, identified as Samples 1 and 13, comprised the testing material. The weight of lignite available was estimated at 310 kg at a predicted 30-35% moisture content, equivalent to 240-250 kg at 15% moisture content. The test program completed by Rheinbraun Consulting GmbH consisted of the following stages:

- Physical/chemical examination of the lignite to determine ash-melting behaviour, reactivity, pore structure, ignition temperature and particle distribution.

**Power energy value taken at 100% efficiency (3.6 GJ/MWh).*

- Cold fluidized-bed tests to determine fluidizing velocity and flow behaviour in the fluidized-bed.
- A hot gasification test to determine the general suitability of the lignite in a fluidized-bed, approximate carbon conversion and product gas composition. These data were used to predict performance of a commercial-scale gasifier feeding Onakawana lignite.

The results of the test program, conclusions and recommendations made by Rheinbraun cannot be provided in this paper for confidentiality reasons. However, it can be stated that Ontario lignite is a suitable feedstock for gasification using the High-Temperature Winkler Process.

PHASE 3 PROCESS UPDATE

The scope of Phase 3 included an update of the Phase 1 process and cost data for the High-Temperature Winkler Process for the base case and options, based on predictions made by Rheinbraun as a result of the test program. These process and cost data were used by the Ontario Energy Corporation for its report to the Ministry of Energy on the conversion of Ontario's indigenous resources of peat, lignite and wood to methanol or other liquid fuels by direct and indirect methods.

The Phase 1 process data for the base case and two coprocessing options were revised to reflect the raw gas composition and yield predicted by Rheinbraun. The process design was also revised to fix the capacity of methanol plant at 2500 t/d for the base case and two options. In Phase 1 the base case and electrolytic hydrogen coprocessing designs were 2010 t/d methanol capacity, and the natural gas coprocessing design was 2780 t/d capacity.

The main impact on the process design was the lower CO and H_2 content in the gasifier-produced raw gas, predicted by Rheinbraun, than that assumed in the Phase 1 design. This lower yield resulted in the following adjustments to the Phase 1 material balance requirements on a per tonne of methanol basis:

	Lignite feed to gasifiers	Natural gas feed	Electrolytic H_2 feed
Lignite only	+11%	Not applicable	Not applicable
Lignite/natural gas	+53%	-8%	Not applicable
Lignite/electrolytic H_2	No change	Not applicable	+30%

The 30% increase in electrolytic hydrogen for the lignite/electrolytic hydrogen option is only partially due to the lower CO and H_2 content of the lignite-derived raw gas. The remainder of the increase results from an optimization of processing units to eliminate an air separation plant (which was included in Phase 1).

The thermal efficiencies, as shown below, fall within the range of that reported by the process developer for the lignite only case and, for the natural gas option, the efficiency is superior to lignite only case and, for the natural gas option, the efficiency is superior to lignite only but lower than the commercially proven efficiency range of 65-67% for a conventional natural gas to methanol process.

Lignite only	46.7%
Lignite/Natural Gas	61.2%
Lignite/Electrolytic H_2	52.1% (31.8%)*

A summary of the capital and operating costs, and total product costs is presented in Table 8. The product costs are given at three capital recovery factors of 10, 15 and 20%. At the lowest capital recovery factor of 10%, respresentative of a public utility investment criterion, the base lignite only case displays a marginally lower product cost than the lignite/natural gas coprocessing option and a significantly lower product cost than the lignite/electrolytic hydrogen coprocessing option. However, with increased capital recovery factors of 15 and 20%, in the range of a private investment criterion, the natural gas coprocessing option appears marginally more favourable than the lignite only case, reflecting the increased capital cost of the lignite only facilities. The lignite/electrolytic hydrogen coprocessing option product costs are still significantly higher than the competing processes at the 15 and 20% capital recovery factors.

PHASE 3 CONCLUSIONS

It was concluded that, if a more detailed technical and financial assessment of an Ontario lignite-to-methanol plant is undertaken, the High-Temperature Winkler (or similar) gasification process be utilized as a component of the overall lignite-to-methanol process for the following reasons:

- The Phase 3 study showed that methanol could be produced for a cost in the order of $290-320/tonne, at a capital recovery factor of 20%, or 23-26 cents/litre. Current methanol price in Ontario is in the order of 18-20 cents/litre (13-14 cents/litre Alberta plant gate plus 5-6 cents/litre transportation cost).
- The bench-scale tests, carried out by Rheinbraun the process developer, indicated that Ontario lignite is well suited to High-Temperature Winkler fluidized-bed gasification.
- The gasifier-produced raw gas composition and yield predicted by Rheinbraun for a commercial plant do not significantly affect the overall process design and final costs developed in Phase 1 and updated in Phase 3 of this study.
- It appears very likely that the High-Temperature Winkler Process will be commercially proven by the study requirement of 1990. A demonstration plant utilizing the High-Temperature Winkler Process is planned to start up in West Germany in later 1984.

In a detailed technical financial assessment of an Ontario lignite-to-methanol plant, two important factors to consider are plant location and representative lignite properties.

The plant location, designated within the scope of this study, is mine-mouth in Onakawana, Ontario. Onakawana is a remote location, accessible only by rail, and is not well suited for construction and operation of a complex lignite-to-methanol processing plant. It may be preferable to locate the plant closer to the marketplace, such as in a serviced industrial area in northern or southern Ontario, where construction and operating costs are likely to be considerably lower. This would entail shipping the lignite, probably dried to 12-15% moisture, to the plant location. This cost is offset by the cost of shipment of 2500 t/d methanol from Onakawana to the marketplace. This alternative is most attractive for the lignite/natural gas coprocessing option since the weight of lignite (12% moisture content) consumed within the plant and methanol produced are almost equivalent.

Two key lignite parameters, moisture and ash content, which have significant impact on the process selection and subsequent costs, were selected at the outset of this study. A moisture content of 45% and an ash content of 18.8% (mf basis) were selected as a result of analyses of grab samples of lignite from one location within the overall Onakawana deposit.

An ash analysis by Rheinbraun on the lignite sample sent for the gasification tests revealed an average ash content of 27.9% (mf basis). Previous analyses performed on Ontario lignite reported moisture contents in the range of 39.7 to 55.2%. A comprehensive sampling and statistical analysis program should be performed on the Onakawana lignite deposit prior to a detailed process and cost evaluation of lignite-to-methanol processes. This program would provide a higher level of confidence in the critical parameters for a lignite-to-methanol process design.

**Efficiency based on a power energy equivalent of 10.5% GJ/Mwh or 34% generation efficiency.*

TABLES

Table 1 – Summary of gasification process characteristics

Commercially proven process	Koppers-Totzek Yes	Lurgi Yes	Westinghouse No	High-temperature Winkler No
Pilot plant or PDU	No; Bench scale only 6 kg/hr; demonstration runs can be arranged at commercial facilities.	No; demonstration runs at Sasol or RUHR-100 facility in Dorsten.	Yes; 35 tonne/day at Waltz Mill, Pa.	Yes; 1 300 kg/hr at Rheinbraun plant, Frechen, West Germany. Small pilot plant at 35 kg/hr.
Experience with lignites	Commercial plant in Greece.	Experience with S. African brown coal and commercial test runs on North Dakota lignite.	PDU test runs with Texas lignite.	Yes; Rhenish Brown coal and North Dakota lignite.
Lignite Feedstock size range and limitations	Pulverized feedstock 90% under 200 mesh; fines can easily be handled.	Optimum size 50 mm × 5 mm; fines not recommended in fixed-bed process.	Ground to 6 mm size; fines can be handled.	Fines to 12 mm size can be handled.
Gasification thermal efficiency/carbon conversion with lignite feedstock*	67-75% 98%	88-95% 97%	83-86% 95%	82% 96%
Lignite moisture content to gasifier	6-8% recommended	30% preferred; min. drying recommended due to fines limitations, 36% max. moisture.	5-15% preferred 24% max.	8-12% preferred 18% max.
Typical gasification agent consumption KG/KG lignite feed at noted moisture content	Lignite Moisture content: 8% Oxygen: 0.73 Steam: 0.14	Lignite Moisture content: 30% Oxygen: 0.20 Steam: 1.10	Lignite Moisture content: 15% Oxygen: 0.45 Steam: 0.20	Lignite Moisture content: 8% Oxygen: 0.542 Steam: 0.167
Expected Syngas composition using lignite as feedstock — % Vol. (major components only)	H_2 : 29.6 CO : 55.9 CO_2 : 11.9 CH_4 : 0.1	H_2 : 38.9 CO : 16.7 CO_2 : 32.0 CH_4 : 11.0	H_2 : 21.70 CO : 35.05 CO_2 : 37.51 CH_4 : 4.53	H_2 : 33.9 CO : 53.1 CO_2 : 9.0 CH_4 : 3.0
Material and Equipment performance	Gasifier refractory problems due to slag attack.	No serious problems noted due to lower temperature operation and extensive commercial experience.	Material selection important due to elevated temperature (950°C) and high-pressure operation (3.1 MPa)	As per Westinghouse
Downstream processing highlights	Extensive compression required due to atmospheric gasification; H_2/CO ratio adjustment required.	Moderate compression as gasification pressure is 3 MPa. No H_2/CO ratio adjustment necessary; however, excessive amount of methane produced.	Moderate compression as commercial gasifier estimated to operate at 3.2 MPa. H_2/CO ratio adjustment required.	Moderate to high compression requirements with gasifier operating at 1.1 MPa. H_2/CO ratio adjustment required.
Environmental requirements	Air – Particulate and acid gas removal. Water – Filtration/flocculation, sour water stripping and Biox. Solids – Ash disposal.	As per Koppers-Totzek, but more extensive waste water treatment i.e., oil separation and phenol removal.	As per Koppers-Totzek.	As per Koppers-Totzek.

* *Comparisons should not be made between processes for thermal efficiency and carbon conversion values given, as gasification parameters and interpretation of results may vary. Also, higher values of thermal efficiency and carbon conversion for a process do not necessarily mean that the process is superior (unwanted carbon products such as CO_2 may constitute the major conversion). Overall thermal efficiency, lignite to methanol is the important parameter.*

Table 2 – Process options

Gasifier	Option	Description	Fuel Grade methanol capacity
			t/d
Koppers-Totzek	Base Case	Lignite only	2010
	Option 1	Lignite-natural gas syngas	2648
	Option 2	Lignite-natural gas H_2	2533
	Option 3	Lignite-electrolytic H_2	2010
Lurgi	Base Case	Lignite only – purge gas SMR	2010
	Option A	Lignite only – purge gas POX	2010
Westinghouse	Base Case	Lignite only	2010
	Option 1	Lignite-natural gas syngas	2227
	Option 2	Lignite-natural gas H_2	2144
	Option 3	Lignite-electrolytic H_2	2010
	Option 4	Lignite-electrolytic H_2 + Cogeneration	2010
High-temperature Winkler	Base Case	Lignite only	2010
	Option 1	Lignite-natural gas syngas	2780
	Option 2	Lignite-natural gas H_2	2835
	Option 3	Lignite-electrolytic H_2	2010

Table 3 – Proximate and ultimate analysis– Onakawana lignite

Proximate analysis, wt %	
Moisture	45.0
Ash, db	18.81
Volatile matter, db	40.49
Fixed carbon, db	40.70
Heating value, Kcal/kg, db	5337.
Ultimate analysis, wt % db	
Carbon	59.30
Hydrogen	3.81
Oxygen	15.97
Nitrogen	.70
Sulphur	1.41
Ash	18.81

This analysis is an arithmetic average of the analyses of two Onakawana lignite samples performed by CANMET.

Table 4 – Base case capital and operating costs
Phase 1

	Koppers-Totzek	Lurgi	Westinghouse	High-temperature Winkler
Methanol capacity, t/y	643 200	643 200	643 200	643 200
Capital cost, $ million	691.2	681.1	639.1	697.6
Capital cost per annual tonne methanol, $/tonne	1074.6	1058.9	993.6	1084.6
Operating cost, $/tonne	119.39	117.69	102.92	109.13
By-product credit, $/tonne	2.34	6.62	3.22	4.22
Total production cost, $/tonne (Operating cost minus by-product credit)	116.75	111.07	99.70	104.91
Total product cost, $/tonne [Production cost + (capital cost/t × per cent capital recovery)]				
at 10% capital recovery	224.51	216.96	199.06	213.37
at 15% capital recovery	278.24	269.91	248.74	267.60
at 20% capital recovery	331.97	322.85	298.42	321.83

Table 5 – Natural gas coprocessing capital & operating costs
Phase 1

	Koppers-Totzek		Westinghouse		H.T. Winkler	
	Option 1	Option 2	Option 1	Option 2	Option 1	Option 2
Methanol capacity, t/y	847 360	802 960	712 640	679 650	889 600	898 690
Capital cost, $ million	533.0	622.9	451.9	536.4	550.2	672.5
Capital cost per annual tonne methanol, $/tonne	629.0	775.7	634.1	789.2	618.5	748.3
Operating cost, $/tonne	162.39	149.44	157.71	143.59	155.43	139.21
By-product credit, $/tonne	.42	.91	.73	1.54	1.04	1.99
Total production cost, $/tonne (Operating cost minus by-product credit)	161.97	148.53	156.98	142.05	154.39	131.09
Total product cost, $/tonne [Production cost + (capital cost/t × per cent Capital recovery)]						
at 10% capital recovery	224.87	226.10	220.39	220.97	216.24	212.05
at 15% capital recovery	256.32	264.88	252.09	260.43	247.16	249.47
at 20% capital recovery	287.77	303.67	283.80	299.89	278.09	286.88

Table 6 – Electrolytic hydrogen coprocessing capital & operating costs
Phase 1

	Koppers-Totzek	Westinghouse		H.T. Winkler
	Option 3	Option 3	Option 4	Option 3
Methanol capacity, t/y	629 130	629 130	629 130	629 130
Capital cost, $ million	655.3	589.0	915.3	629.2
Capital cost per annual tonne methanol, $/tonne	1041.6	936.2	1454.9	1000.0
Operating cost, $/tonne	161.80	148.77	119.52	167.52
By-product credit, $/tonne	1.74	2.18	2.18	2.85
Total production cost, $/tonne (Operating cost minus by-product credit)	160.06	146.59	117.34	164.67
Total product cost, $/tonne [Production cost + (capital cost/t × per cent Capital recovery)]				
at 10% capital recovery	264.22	240.21	262.89	264.67
at 15% capital recovery	316.30	287.02	335.58	314.67
at 20% capital recovery	368.38	333.83	408.32	364.67

Table 7 – Partial oxidation/steam reforming capital and operating costs
Phase I

	LURGI	
	Base Case Steam Reforming	Option A Partial Oxidation
Methanol capacity, t/y	643 200	643 200
Capital cost, $ Million	681.1	687.5
Capital cost per annual tonne methanol, $/tonne	1058.9	1068.9
Operating cost, $/tonne	117.69	120.17
By-product credit, $/tonne	6.62	6.62
Total production cost, $/tonne (Operating cost minus by-product credit)	111.07	113.55
Total product cost, $/tonne [Production cost + (capital cost/t × per cent capital recovery)]		
at 10% capital recovery	216.96	220.44
at 15% capital recovery	269.91	273.89
at 20% capital recovery	322.85	327.33

Table 8 – Summary of capital, operating and product costs
Phase 3, H.T. Winkler process

	Feedstock Cost	Lignite only	Lignite/natural gas coprocessing	Lignite electrolytic H_2 coprocessing
Methanol capacity, t/y		800 000	800 000	800 000
Capital cost, $ million		859.9	581.1	786.5
Capital cost per annual tonne Methanol (MeOH), $		1074.4	726.4	983.1
Feedstock cost, $/t MeOH				
Lignite	$15.00/t	59.62	22.50	35.87
Natural gas	$0.156/Nm^3	--	86.62	—
Power (for Electrolytic H_2)	2.71c/kW hr	—	—	109.75
Other operating costs, $/tonne		47.37	37.51	35.12
By-product credit, $/tonne		4.61	1.57	2.82
Total production costs, $/tonne (Operating cost minus By-product credit)		102.38	145.06	177.92
Total product cost				
at 10% capital recovery		209.82	217.70	276.23
at 15% capital recovery		263.54	254.02	325.38
at 20% capital recovery		317.26	290.34	374.54

FIGURES

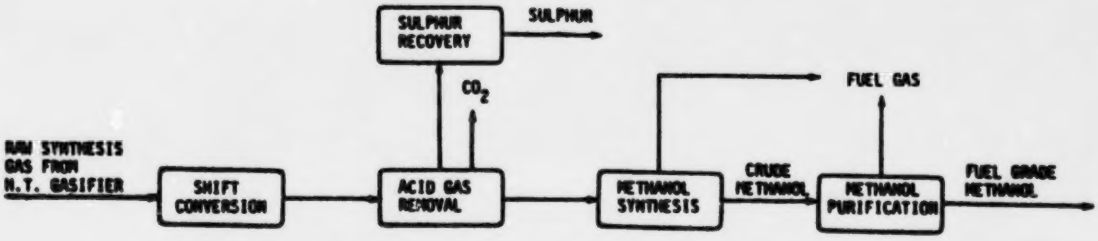
SULPHUR RECOVERY
SULPHUR
CO_2
FUEL GAS
RAW SYNTHESIS GAS FROM H.T. GASIFIER
SHIFT CONVERSION
ACID GAS REMOVAL
METHANOL SYNTHESIS
CRUDE METHANOL
METHANOL PURIFICATION
FUEL GRADE METHANOL

Fig. 1 – Methanol production from high-temperature coal gasifier raw synthesis gas – base case

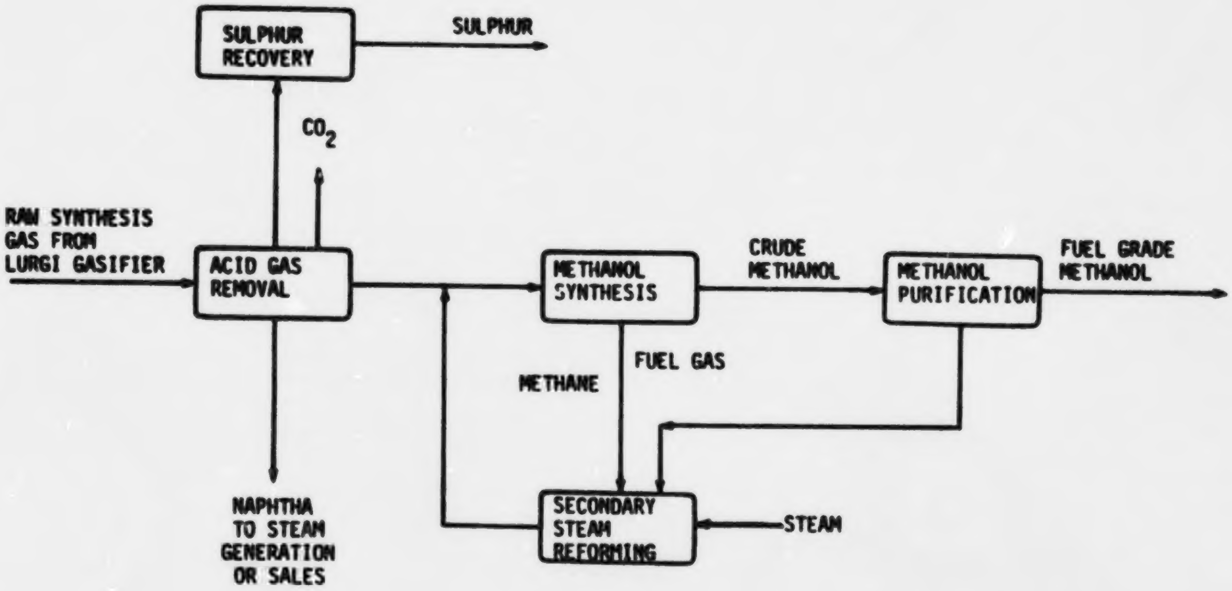
SULPHUR RECOVERY
SULPHUR
CO_2
RAW SYNTHESIS GAS FROM LURGI GASIFIER
ACID GAS REMOVAL
METHANOL SYNTHESIS
CRUDE METHANOL
METHANOL PURIFICATION
FUEL GRADE METHANOL
FUEL GAS
METHANE
NAPHTHA TO STEAM GENERATION OR SALES
SECONDARY STEAM REFORMING
STEAM

Fig. 2 – Methanol production from Lurgi gasifier raw synthesis gas

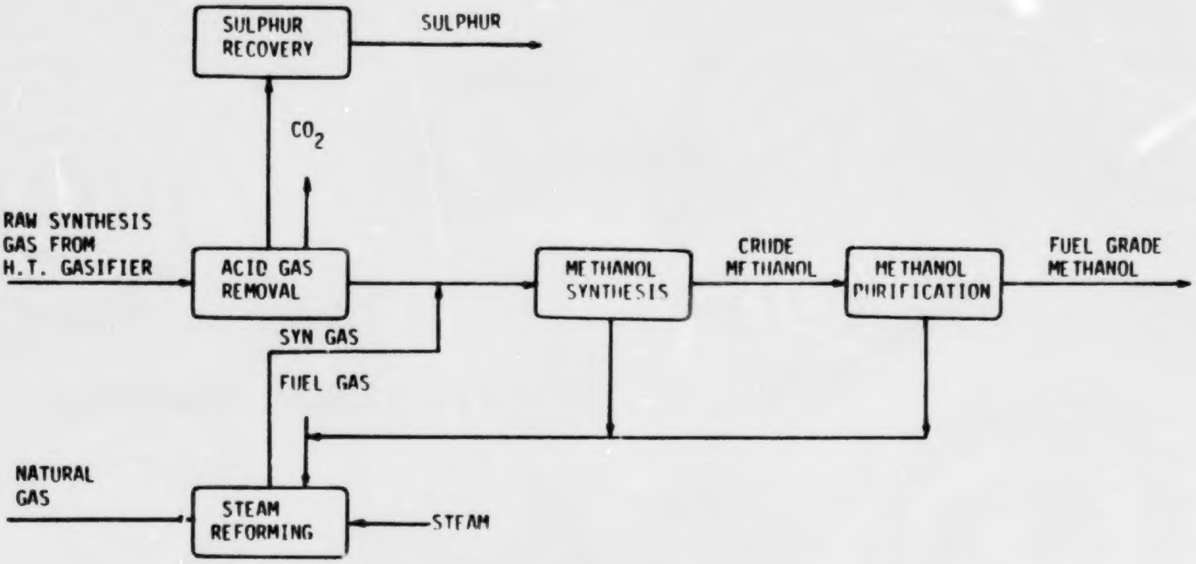
SULPHUR RECOVERY
SULPHUR
CO_2
RAW SYNTHESIS GAS FROM H.T. GASIFIER
ACID GAS REMOVAL
METHANOL SYNTHESIS
CRUDE METHANOL
METHANOL PURIFICATION
FUEL GRADE METHANOL
SYN GAS
FUEL GAS
NATURAL GAS
STEAM REFORMING
STEAM

Fig. 3 – Methanol production from high-temperature coal gasifier raw synthesis gas – Option 1

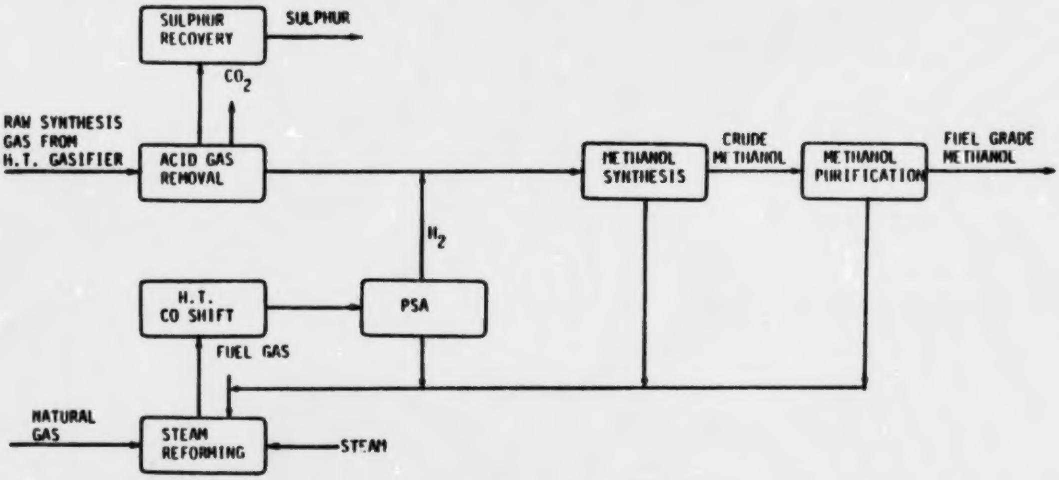
SULPHUR RECOVERY
SULPHUR
CO_2
RAW SYNTHESIS GAS FROM H.T. GASIFIER
ACID GAS REMOVAL
METHANOL SYNTHESIS
CRUDE METHANOL
METHANOL PURIFICATION
FUEL GRADE METHANOL
H_2
H.T. CO SHIFT
PSA
FUEL GAS
NATURAL GAS
STEAM REFORMING
STEAM

Fig. 4 – Methanol production from high-temperature coal gasifier raw synthesis gas – Option 2

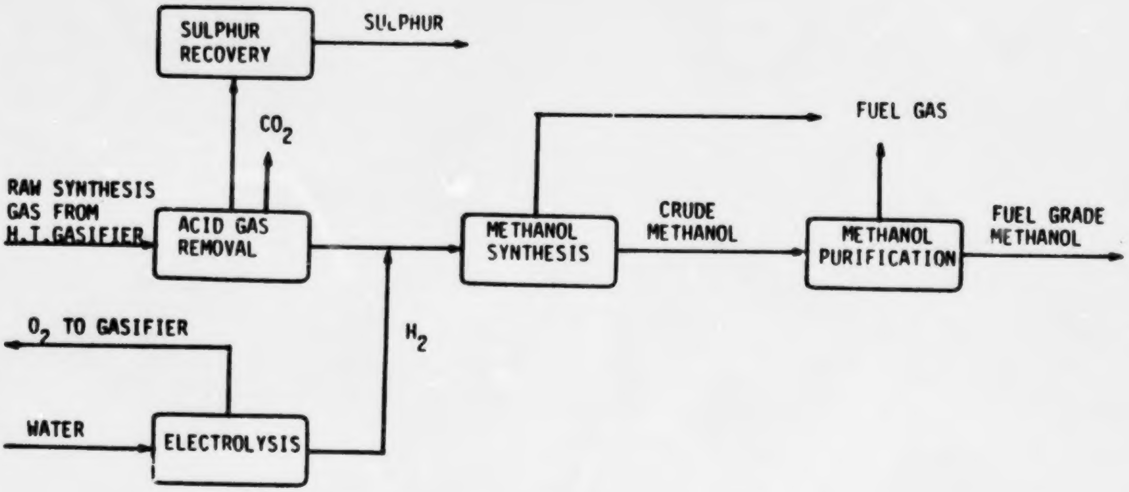
SULPHUR RECOVERY
SULPHUR
CO2
FUEL GAS
RAW SYNTHESIS GAS FROM H.T.GASIFIER
ACID GAS REMOVAL
METHANOL SYNTHESIS
CRUDE METHANOL
METHANOL PURIFICATION
FUEL GRADE METHANOL
O2 TO GASIFIER
H2
WATER
ELECTROLYSIS

Fig. 5 – Methanol production from high-temperature gasifier raw synthesis gas – Option 3

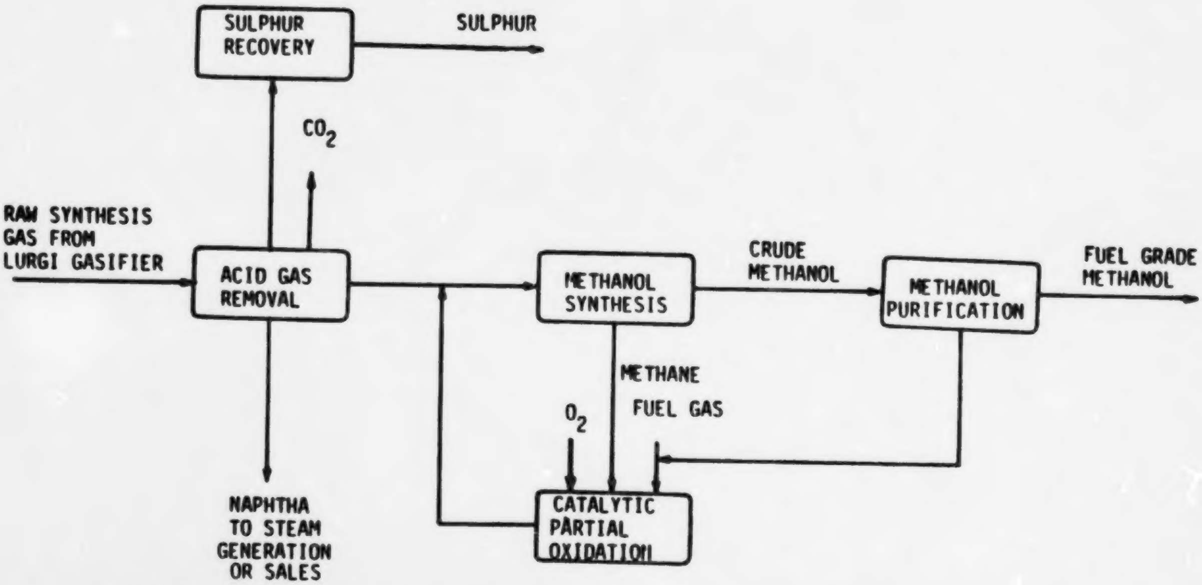
SULPHUR RECOVERY
SULPHUR
CO2
RAW SYNTHESIS GAS FROM LURGI GASIFIER
ACID GAS REMOVAL
METHANOL SYNTHESIS
CRUDE METHANOL
METHANOL PURIFICATION
FUEL GRADE METHANOL
METHANE
O2
FUEL GAS
NAPHTHA TO STEAM GENERATION OR SALES
CATALYTIC PARTIAL OXIDATION

Fig. 6 – Alternate process for methanol production from Lurgi gasifier raw synthesis gas – Option A

SESSION IV: PAPER 17

COAL TO GASOLINE – IS IT ECONOMIC?

*M. Taherzadeh**
Petro-Canada Products Inc.

ABSTRACT

The Western Canada Coal Liquefaction study which began in 1980 concluded (in early 1982) that the economics of direct coal liquefaction processes were unattractive, and there would be little to gain by continuing work in that direction. However, the prefeasibility stage of the study was extended to consider the conversion of coal rejects to transportation fuels via an indirect route.

The major incentive for the proposed indirect route was the economic advantage in converting a low-value coal feedstock to a high-value petroleum liquid product.

Samples of the designated coal rejects were tested and evaluated by two different gasification process developers. Results confirmed the technical feasibility of gasification of coal rejects and production of synthesis gas. After a brief process comparison, a gasification process was selected. Subsequently, the coal-to-gasoline complex was conceptually designed and capital and operating costs were estimated.

Preliminary *Base Case* economic analysis indicated a reasonable after-tax DCF rate of return, and a relatively short pay-back period.

The project economics compare favorably with any of the past or present tar-sand and heavy oil synthetic crude projects. Furthermore, it provides advantages in the areas of capital cost and product slate. Considering the preliminary technical feasibility and the reasonable Base Case DCF rate of return, the project proceeded to its second phase for detailed technical and economic evaluation.

Of course, these conclusions were based upon business/economic assumptions which were appropriate at the time (early 1983) but have not been updated for the more pessimistic outlook today. Hence current economic returns may be somewhat lower.

**denotes speaker*

PRÉSENTATION 17

LA CONVERSION DU CHARBON EN ESSENCE: PROCÉDÉ RENTABLE?

*M. Taherzadeh**
Les produits Pétro-Canada Inc.

RÉSUMÉ

L'étude portant sur la liquéfaction du charbon candien de l'Ouest commencée en 1980 a démontré au début de 1982 que les procédés de liquéfaction directs étaient de peu d'intérêt et qu'il était superflu de poursuivre des travaux en ce sens. Cependant, le stade préparatoire des études de faisabilité a été prolongé pour permettre l'étude de la conversion des rebuts de charbon en combustibles au moyen d'une méthode indirecte.

L'élément principal qui a motivé le choix d'un procédé indirect repose sur les avantages économiques liés à la conversion d'une matière première à faible teneur en charbon à un produit liquide à haute teneur en pétrole.

On a fait le contrôle et l'évaluation d'échantillons de rebuts de charbon sélectionnés à l'aide de deux procédés de gazéification différents. Les résultats ont démontré que la gazéification des rebuts de charbon et la production du gaz de synthèse étaient techniquement possibles. Après une brève comparaison des procédés de gazéification, on en sélectionna un. Ensuite, on élabora les plans d'une installation de conversion du charbon en essence et on fit l'appréciation des coûts en immobilisations et des coûts de fonctionnement.

Des analyses préliminaires d'un cas d'espèce indiquent un taux de rendement actualisé raisonnable après imposition et un délai de récupération relativement court.

Les perspectives économiques du projet se comparent favorablement à celles de tout projet actuel ou antérieur de conversion de sable asphaltique et de pétrole lourd en pétrole synthétique. En outre, le projet est rentable au niveau de la production et des coûts en immobilisations. Comme ce projet semble techniquement possible et que le taux de rendement actualisé après imposition est raisonnable comme l'indique l'étude du cas d'espèce, on a entrepris la deuxième phase de l'appréciation technique et économique du détail de ce projet.

Bien entendu, ces conclusions découlent des perspectives économiques qui prévalaient à l'époque (début de l'année 1983) mais qui ne correspondent plus aux perspectives plus sombres aujourd'hui. Par conséquent, il est possible que les retombées économiques soient moindres.

**indique le conférencier*

COAL TO GASOLINE – IS IT ECONOMIC?

INTRODUCTION

British Columbia has some of the largest coal reserves in Canada. The majority of its reserves are low-sulphur bituminous coals and are mineable by relatively cheap open-pit methods.

Coal conversion into synthetic fuels can make a very significant contribution to alleviating energy needs, particularly in satisfying those market sectors, such as transportation, where there are no readily available near-term substitutes for energy in liquid form, and which are so vital to the nation's economic well-being.

Since more than 75% of B.C.'s current oil requirements are imported, the potential for liquefying coals into petroleum substitutes deserves a thorough investigation.

Recognizing this potential, the Western Canada Coal Liquefaction Consortium was formed to initiate the development of a coal-based synthetic liquid fuels industry in British Columbia.

The consortium conducted a prefeasibility study and assessed the technology and economics of converting bituminous coals from Monkman and Sparwood areas of British Columbia into transportation fuels via direct coal liquefaction processes. The results of this prefeasibility study indicated that the principal impediments in getting the synthetic fuel to the market are:

- economics
- environmental
- regulatory.

Since both the environmental and regulatory aspects exert some direct and/or indirect influence on costs, the problem can be reduced to one overriding factor, project economics – synthetic fuels simply are expensive to produce. Economic analysis indicated that there are three major areas of sensitivity:

- feedstock cost
- product value
- capital charges.

Decreasing the feedstock cost has a marked upward effect on the rate of return and, conversely, reducing the forward value of the products reduces the rate of return.

Reduction in capital charges for the sake of improving the rate of return is an almost impossible task. A main characteristic of all major synthetic fuel plants is their capital intensity, since the raw materials (coal, tar sands, or shale oil) are solid and more costly to process than liquids.

In the area of product value, the outlook, of course, depends on perceptions of the cost of synthetic fuels compared to the prices they will command. These perceptions will be those of industry leaders, government officials, and those responsible for the arrangement of project financing. However, the prices obtainable would depend mainly on the price of the internationally traded crude oil products and the levels at which the government is willing to provide price guarantees.

It was therefore felt that the only factor which could propel the project to produce a more reasonable rate of return is the lower feedstock cost. This could perhaps be achieved by selecting the low-value coal rejects as the proposed feedstock. An indirect coal liquefaction process route was then considered for its proven commerciality and less sensitivity toward feedstock properties. The overall incentive for the proposed project was the economic potential of converting a low-value coal feedstock to a high-value hydrocarbon liquid product.

FEEDSTOCK PROPERTIES

The coal rejects produced by the B.C. Coal Elkview Preparation Plant at Sparwood, British Columbia have been selected as the feedstock for the coal-to-gasoline complex.

The Elkview plant produces four separate reject streams (with different compositions) all of which would be utilized as feedstock to the coal conversion plant.

The feedstock has the unique combination of the following characteristics:

- high ash content
- relative high-heating value
- medium reactivity
- low cost
- large reserves, accumulated over ten years and increasing at 1.8 to 2.5 million t/a.

The ultimate analysis of the feedstock is shown in Table 1.

GASIFICATION TESTING

The objective was to establish the technical feasibility of gasifying the coal rejects using two gasifiers: Texaco and Koppers-Totzek. These two gasification technologies were considered the most suitable for producing synthesis gas from the coal rejects.

An elaborate and tedious procedure was then used to collect a representative and sufficient coal sample. The ultimate analysis of the coal sample showed the following results.

A portion of the collected sample was forwarded to both gasification developers for their evaluation and prediction of the synthesis gas yield. The laboratory gasification testing of the designated coal by Texaco concluded that the ash fusion properties of the coal would necessitate operation at too high a temperature. As a result they recommended the use of up to 4.5% fluxing agent to reduce the ash fusion temperature of the coal feedstock.

The evaluation by GKT (Gesellschaft Fur Kohle-Technologie MbH), which represents the Koppers-Totzek gasification process developer, also indicated the need for use of fluxing agent. However, because of the higher normal operating temperature of the Koppers-Totzek gasifier, only 0.1% flux is required.

Both developers predicted a fairly high yield of synthesis gas. However, their predictions were significantly different in terms of H_2/CO ratio.

PROCESS COMPARISON, EVALUATION AND SELECTION

The selected indirect route was the gasification of coal to synthesis gas, conversion of synthesis gas to methanol and conversion of methanol to gasoline. In a coal-to-gasoline complex, selection of the gasifier for production of synthesis gas has the greatest impact on the overall project feasibility both in terms of technical and economic considerations. Selection of the upstream/downstream processes is much easier and they have a lesser impact on the project. This is mainly due to their widespread use in other industries, and the availability of more reliable technical and economic information on their performances.

Two gasifiers, Texaco and Koppers-Totzek, were compared on the basis of information obtained under a secrecy agreement from their developers. The overriding critierion was to select the gasifier with the least technical uncertainty so that an accurate cost estimate based on realistic data could be prepared.

The overall yields for conversion of coal to gasoline based on the two gasifiers are summarized in Table 2.

The Texaco gasifier can be seen to produce a higher liquid hydrocarbon yield per tonne of coal with a slightly higher consumption of oxygen and process water.

The operation of the gasifiers themselves, from both technical and commercial standpoints, has been assessed numerically against several criteria, each of which has been allocated a weighting. The overall evaluation is shown in Table 3. As can be seen the numerical evaluation scores heavily in favour of the Koppers-Totzek gasifier. The principal determining factors are:

- the lower technical risk
- the higher service factor
- the proven commercial operation.

On the basis of this comparison it was decided that the Koppers-Totzek gasifier would be used in this study to develop the capital and operating costs of the coal-to-gasoline complex. It should be stressed that this is not a final selection committing the project consortium to installing a Koppers-Totzek gasifier should the project proceed to completion. It is simply the choice that provides the most realistic estimate of the overall costs of the process based on the preliminary data that have been collected to date.

CONCEPTUAL DESIGN OF THE COAL-TO-GASOLINE COMPLEX

The conceptual design of the coal-to-gasoline complex is based on the conversion of coal rejects to gasoline and LPG. The principal process steps are:

1. Gasification of the coal to produce synthesis gas.
2. Modification of the synthesis gas (H_2/CO) ratio and removal of acid gas impurities.
3. Production of crude methanol from the treated synthesis gas.
4. Conversion of the methanol to gasoline and LPG using the Mobil MTG Process.

The design is based on the complete utilization of the coal reject output of the Elkview plant to produce:

- 5250 T/D raw methanol intermediate
- 1818 T/D (16126 bbl/d) gasoline
- 340 T/D (3536 bbl/d) LPG.

There are several areas of the process flowsheet where assumptions as to major process operating conditions and preliminary process selections had to be made to permit the development of the overall design. While these assumptions produce a design that is viable, it is almost certainly not optimal and would require further evaluation in a more detailed study.

The overall process flowsheet is shown in Figure 1. Coal rejects are received from the Elkview Plant, then crushed and dried in the coal preparation plant. The coal dust is fed with oxygen and steam, to the Koppers-Totzek gasifier.

The gasifier raw gas is compressed to 6900 kPa and fed to the CO shift reactors. The gases are then passed through the Rectisol acid gas removal plant to remove hydrogen sulphide and most of the carbon dioxide. The hydrogen sulphide rich off-gas is routed to the Stretford plant for sulphur recovery.

The clean synthesis gas is further compressed, combined with recycle hydrogen from the PSA unit and fed to the methanol synthesis loop. The synthesis loop purge gas is sent to the PSA plant for hydrogen recovery. The crude methanol is passed forward to the Mobil MTG plant for the synthesis of gasoline. The methanol is converted to LPG and light and heavy gasoline. The heavy raw gasoline fraction is passed to a hydrotreating unit to reduce its durene content. The treated heavy gasoline and other MTG products are sent forward for blending and storage.

The approximate products qualities are shown in Tables 4 and 5.

MANPOWER REQUIREMENTS AND CONSTRUCTION SCHEDULE

Operating labour

The estimated operating labour force is 300 men. Supervision is not included in this total but is added as a factor in the development of the operating costs.

Maintenance Labour

The maintenance labour force has been estimated as 450 men. The estimate is based on the calculation of total overall maintenance costs as a percentage of plant capital costs.

Construction Schedule

It is anticipated that construction schedule of the complex will be dictated by the time required to field fabricate the gasifiers required. It is estimated that 45 to 48 months will be needed to complete the construction of the gasification facility. Therefore, the overall construction period for the whole complex is estimated to be 48 months.

COST ESTIMATES

The capital and operating costs for the coal-to-gasoline complex have been calculated using specific estimates from vendors backed up by in-house data derived from earlier projects. Typical industrial cost estimates at this level of design have accuracies in the range of ±30%. A conscious attempt has been made to produce an overall cost estimate that is conservative. The more poorly defined an area (for example, the water treatment plant) the more conservative the cost estimate for that area has been made. Some of the bases and assumptions used for developing the capital and operating costs, and economic evaluation are tabulated in Table 6.

For data not presented in first quarter 1983 Canadian dollars for a S.E. British Columbia location, the conversion factors have been used (Table 6).

The capital cost estimate of $1.42 billion is summarized in Table 7. All manpower have been charged at $34,000 per annum. The combined operating and maintenance labour charge has been increased by:

- 15% for supervision
- 35% for payroll burden and administrative overhead.

Operating materials are charged at 15% of operating labour.

ECONOMIC ANALYSIS

The objective was to establish the general project economics as well as determine which factors were most important economically. An attempt was made to estimate some of the contingencies or sensitivities which would significantly impact project economics.

The bases and assumptions used in developing the project economics are summarized in Table (6). Other parameters used are outlined below.

Fixed capital costs were estimated in the previous section and are summarized as follows:

Fixed Capital $MMCDN (1Q 1983 Basis)

Process Equipment	911
Utilities	108
Offsites	124
Prepaid Royalties	3
Fixed Capital	1146
Contingency at 15%	172
Total Fixed Capital	1318

Working capital for the purposes of taxation is estimated as follows:

$ Million (1983 Basis)

Coal Supply, 30 days	1.6
Finished Product supply 15 days at Cash Cost of Production	8.2
Cash Requirements, 1 month of payroll + plant overhead/administration	4.2
Catalysts, 6-month supply	5.5
Spares/Warehouse, 2% of installed carpet	26.3
	45.8

Working Capital requirements are inflated by the CPI Index.

The selling price for *unleaded gasoline projections* is based on two factors, the price of crude oil and the ratio of unleaded gasoline to crude oil. The crude oil forecast is based on:

- a $2.00 US/bbl increase in prices in 1984 from current levels
- no increase in 1985
- increase with inflation through 1987
- 1% per year real growth thereafter.

The difference between international prices and Canadian blended price will narrow to about 5% by 1990 and 3% by 1995.

Based on 1982 data, the ratio of unleaded gasoline (net at the refinery) to crude acquisition cost is about 1.37 in the Vancouver area, based on refinery net price of $.30 per litre and crude costs of $34.75.

Prices for *propane and butane* were derived from the in-house data. These are based on forecasts of U.S. prices, as much of the LPG produced in western Canada is sold in the U.S. Transportation costs have been included, assuming export to the U.S. These prices, particularly propane, show increases greater than crude oil based on relatively modest supply increases and demands for petrochemical and premium fuel uses. The LPGs are projected to provide approximately 10% of the project revenue.

Manufacturing Costs

The manufacturing costs used in the economic calculations are shown in Table 8. Manufacturing costs are estimated to escalate at the Consumer Price Index rate of 6.5% per year average.

Government Support

Experience with major synfuels projects, both in Canada and the U.S., has indicated that some sort of government support is generally required. This stems from the high *up-front* capital requirement, uncertainty with respect to energy pricing/policy and technological and other risks. It implies that the project is supporting national and/or provincial policy as well as serving commercial purposes. Assistance may come in a number of forms, such as loan guarantees, direct capital injections, and/or tax relief or adjustment.

Because the principal product is gasoline, as opposed to a resource product such as synthetic crude oil, a somewhat different approach was taken to estimate government support for the base case economics. This is to assume that money from the federal and B.C. provincial governments' gasoline taxes on the product could be applied to the project as a subsidy for the life of the project. The specific taxes were (1983):

	¢/Litre Gasoline
Federal Excise Tax	1.50
Federal Sales Tax	3.15
Total Federal	4.65
B.C. Fuels Tax	6.88
Total Tax	11.53

This amounts to about 38% of the net price at the refinery. It should be noted that in the above calculations the governments do not 'lose' all the fuels taxes they eliminate, as that money is treated as additional revenue and therefore provides additional income taxes.

Base Case Analysis

The economics calculated on the base case parameters noted above are:

CDF Rate-of-Return	17.5%
Payback period (excluding construction period)	5 years

The following observations can be made on the base case calculations.

At 17.5%, the base case DCF rate-of-return would generally be good enough for the project to be seriously considered, though the specific *hurdle rate* depends on the type of project, expected interest/inflation rates, and the particular company. The current reduction in interest and inflation rates will likely reduce rate-of-return requirements over time. When compared with the projected long-term average rate of inflation of 6.5% per year, the 'real' (inflation adjusted) rate of return is about 11% after tax. This too would generally rate the project for serious consideration.

The cumulative net cash flow profile, shown in Figure 2, indicates a maximum cash exposure of about $1.1 billion at the end of the construction period and a project payback of nine years from start of construction. This is due to the large 'up-front' capital requirements, along with the four-year construction period. The relatively long payback periods are generally typical of capital-intensive synthetic fuels projects and a key reason why government support in some form is frequently required for these projects. Of course, by staging the construction of the complex, the large up-front capital requirement could be reduced. This is possible due to the modular nature of the complex.

Supporting the above, the capital cost per daily effective bbl of capacity is about $67,000 (1983 basis). This is in the same order of the cost of a tar sand plant plus its refinery (for production of final products). As an example the combined capital cost per daily effective bbl for the Syncrude Canada plant in Fort McMurray and Shell Scotford refinery is approximately $100,000 (1983 basis). While a direct comparison may not be appropriate because of different product slates, etc., a general comparison emphasizes similar high up-front costs of this type of project.

SENSITIVITY ANALYSIS

In addition to the base case, economics were developed for a series of alternate cases, or *sensitivities*, in order to test the impact of key parameters. This is especially important in analyzing this type of project because the extended time frame, new technology and preliminary costing make it difficult to tie down the key parameters with much certainty.

The sensitivities examined include:

- general sensitivities of selling price, capital costs and operating costs
- two cases to determine what impact alternative federal/provincial government support levels might have on the project
- an economic scenario with higher energy prices and higher inflation rates
- a case assuming financing via 50% debt/50% equity.

The basic sensitivities of selling price, capital cost and manufacturing costs were calculated and are shown in Figure 3. This figure shows the impact on project DCF when one of the key factors changes from base case projections by a specific percentage.

The existence and level of government support is very important in the project economics. Two sensitivities were run with regard to government support and are summarized below with the resultant economics:

- If there were no government assistance at all, the project would provide an 11% DCF with an eight year payback (excluding the construction period), assuming other base case parameters were used.
- If the gasoline tax were flowed to the project until payback was achieved, then cut off and returned to the government, the project would provide a DCF return in the 14 to 15% range with a payback of five years.

A specific sensitivity was developed to include a higher energy price/higher economic environment. In this case the CPI averages 7.5% per year with construction inflation at 10%. International crude prices are generally based on a 'high case' scenario which, starting from the current price, assumes a 1% per year real growth through 1987 and 2% growth thereafter. The DCF in this case is approximately 19%. The positive impact of the higher energy prices is somewhat offset by the effects of inflation on capital and operating cost.

Previous economics have been calculated on a 100% equity basis. This is appropriate for project evaluation. However, a project of this type would normally include debt financing, and the leverage created would increase the return on equity to the sponsor though it would also increase the risk.

Based on a capital structure of 50% debt/50% equity, and assuming an average interest rate of 10%, return on the equity would increase to about 19% depending on repayment schedule.

CONCLUSIONS

The results of this feasibility study show that the economic potential of this project is such that the undertaking of its further phases should be seriously considered. There is a clear indication that the project, as it was considered, was technically feasible and economically sound. The study has also demonstrated that the indirect coal liquefaction process under consideration is not only competitive with Tar-sand and Heavy Oil projects being considered but also provides some advantages regarding size and final product.

The study also concludes that:

- The designated coal feedstock can be gasified with a high yield of synthesis gas.
- Proven commercial processes exist to convert the coal to gasoline as final product.
- The products are in a finished form and are marketable without any further processing.
- Analysis of the Base Case economics indicated an after-tax DCF rate of return of 17.5% with a five-year payback period (excluding the construction period).

- Changes in the major economic parameters of 20% would leave the economics in the 15 to 20% DCF range.
- Some degree of government support is required to keep the DCF at 17.5%. Without this support the project would provide an after-tax DCF of 11%.
- The high Base Case DCF rate of return of 17.5% justifies proceeding to the 2nd phase and further detailed analysis of the project.
- The economic projection was based on the criteria existing in 1983. Since then those criteria have changed somewhat. Therefore the economics should only be considered as guidelines, providing general direction and pinpointing areas to focus attention on and better define.
- The project will generate socio-economic benefits within the east Kootenay region of B.C. and the southwest corner of Alberta. It is estimated that a peak construction work force of 4000 will be reached during 3-4 years of construction, with a permanent staff of 750.
- Finally, the cursory environmental overview which was undertaken during this phase of the study did not indicate any significant impact on the region.

ACKNOWLEDGEMENT

The Western Canada Coal Liquefaction Consortium wishes to thank Energy, Mines and Resources Canada for its technical and financial support for this study.

TABLES

Table 1 – Ultimate analysis (MF) %wt

Carbon	50.74
Hydrogen	2.99
Nitrogen	0.65
Sulphur	0.05
Chlorine (wt ppm)	74
Ash	40.53
Oxygen (by diff.)	5.04
Measured gross heating value (MF)	21 113 KJ/kg (9077 BTu/lb)

Table 2 – Gasifier comparison, gasoline and LPG yield

Feed	Gasifier	
	Texaco	Koppers-Totzek
Coal Feed MT/D	9 600	9 600
Oxygen Feed MT/D	6 500	5 370
Water Feed KG/HR	179 000	136 000
Products:		
Methanol produced MT/D	5 200	4 980
Gasoline produced bbl/D	16 700	16 000
LPG produced bbl/D	3 400	3 250
Total products bbl/D	20 100	19 250
Ash + Slag produced MT/D	4 400	3 900

Table 3 – Gasifier comparison, overall evaluation

	Weight	Texaco	Koppers-Totzek
Technical Factor			
– Process Related	1.0	7	8.5
– Technical Risks	3.5	5.4	9.2
Commercial Factor			
– Service Factor	3.5	7	9.5
– Environmental	1.0	9	9
– Proven Experience	1.0	5	10
Total	10	64	93

Table 4 – Estimated properties of blended gasoline

Gravity, °API	64
Octane Numbers	
Research, clear	93
Motor, clear	83
(R+M)/2, clear	88
Reid Vapor Pressure, psi	10
Distillation, °F	
IBP	88
10%	116
30%	156
50%	212
70%	280
90%	313
EP	400
Composition, vol.%	
Paraffins	52
Olefins	16
Napthenes	5
Aromatics	27
Durene Content, wt %	2
Molecular Weight	94

Table 5 – Typical propane/butane LPG compositions

Component	Propane Vol. %	Mixed Butane Vol. %
Ethane	4.0	—
Propylene	3.7	—
Propane	90.5	0.1
Isobutane	1.7	74.2
Butenes	0.1	8.1
Butane	—	17.4
Pentanes	—	0.2

Table 6 – Economic basis and assumptions

$ Basis	First Quarter 1983 Cdn$
No. of operating days	330 D/y
Construction start/finish	1986/1990
Operating Life	20Y
Financing	100% Equity
Federal/Prov. Tax Rate	48%
1 Cdn$	$0.82 U.S.
Cap. Cost Allowance & Inv. Tax Cred. (for 3 years)	10%
Inflation Rate (Cons. Price index)	6.5%/Y
Inf. Rate for Equip/Const.	9%/Y
Prepaid Royalties	2% of TIC
Start-up Costs	5% of TIC
Contingency	15% of TIC
Working Capital	2% of TIC
Manpower Charges	$34,000/Y
Project Sponsors Taxation Status	Currently Taxable
Spending Profile Year 1	10%
Year 2	35%
Year 3	40%
Year 4	15%
Plant's Production Capacities:	
unleaded gasoline	5,322,000 bbl/y
Butane	757,000 bbl/y
Propane	410,000 bbl/y
Location Allowance:	– 10% relative to U.S. Mid-West – 20% relative to U.S. Gulf Coast – 20% relative to West Germany

Table 7 – Coal-to-gasoline complex – capital cost summary
Basis MM$CDN 1st Quarter 1983

	Total installed Cost	Prepaid Royalty (1)	Start-up Cost (2)	Total Plant Investment
Process Units				
Coal Preparation	40	N/A		
Air Separation	160	(4)		
Gasification	240	(4)		
Raw Gas Compression	53	N/A		
CO Shift	60	1.2		
Rectisol Acid Gas Removal	63	(4)		
Stretford Sulphur Plant	9	0.2		
Methanol Synthesis	96	1.9		
Hydrogen PSA Unit	8	(4)		
MTG Plant	182	N/A		
	911	3.3	45.6	959.9
Utilities				
Refrigeration	11	N/A		
Boiler/Superheater	10	N/A		
Cooling Water System	12	N/A		
Water Treatment	75	N/A		
	108	0	5.4	113.4
Offsites				
Storage/Blending	20	N/A		
General Facilities (3)	104	N/A		
	124	0	6.2	130.2
Subtotals	1143	3.3	57.2	1203.5
Initial Chemicals & Catalysts				22.0
Contingency (15% of TIC)				171.5
Working capital (2% of TIC)				23.0
				1420.0

Notes: (1) Prepaid royalty at 2% TIC where applicable
(2) Start-up cost at 5% of TIC
(3) General facilities at 10% of TIC
(4) Denotes royalty included in TIC

Table 8 – Manufacturing costs

Variable Costs	$ MILLION	% of Total
Coal at $6/tonne	19	11
Power at 2¢/KWH	39	22
Catalysts	Confidential	Confidential
MTG process royalty	Confidential	Confidential
Total variable cost including Catalyst and royalties	93	53
Fixed Costs		
Operating labour (300 emn at $17/hr total)	10	6
Supervision	4	3
Maintenance materials/Labour (450 men)	32	18
Plant overhead	9	5
Insurance/Property tax at 2% fixed cap.	26	15
Total fixed cost	81	47
Total cash manufacturing costs	174	100

FIGURES

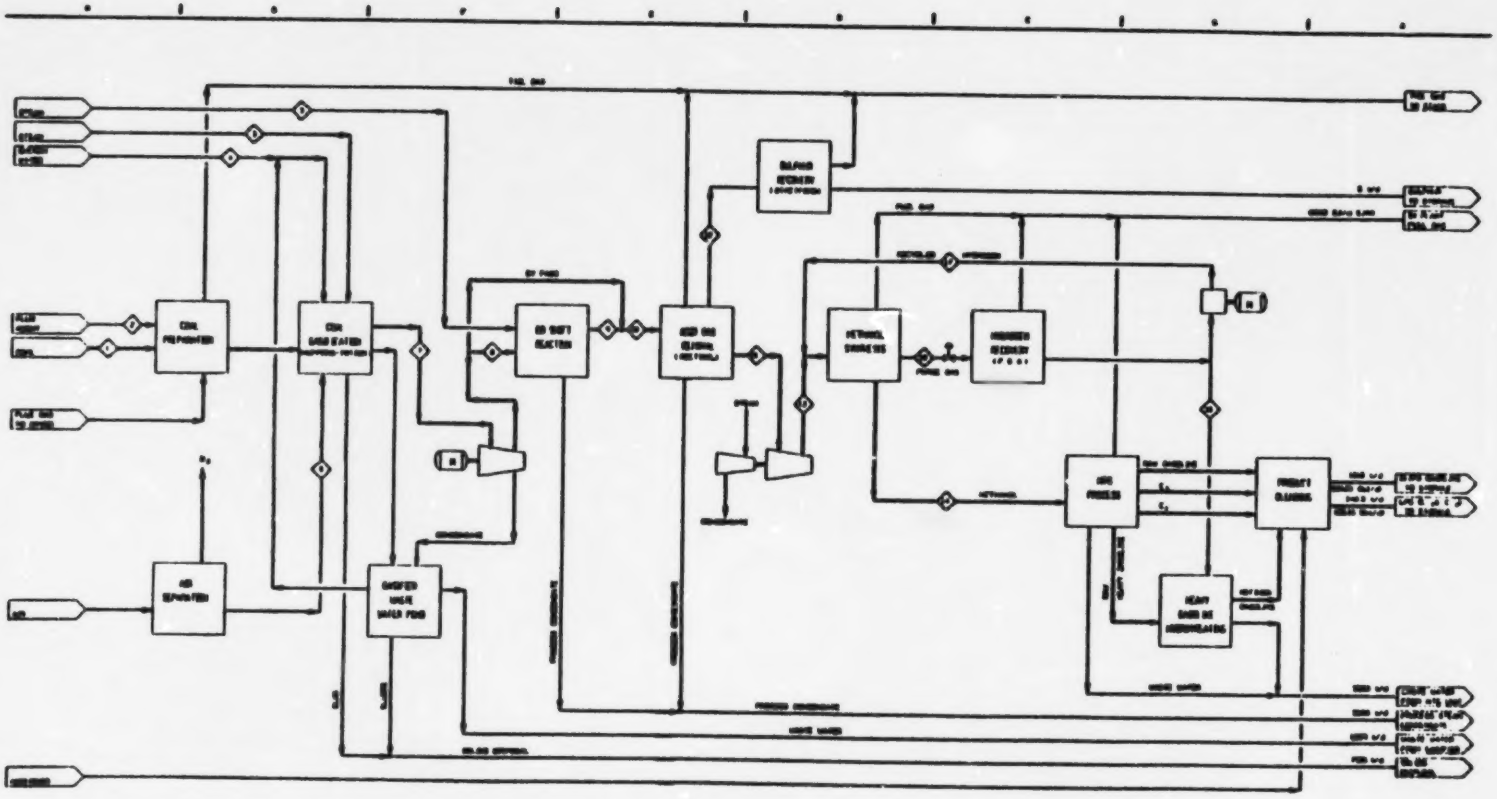
COAL PREPARATION
COAL GASIFICATION
AIR SEPARATION
GASIFIER WASTE WATER POND
CO SHIFT REACTOR
ACID GAS REMOVAL
SULFUR RECOVERY
METHANOL SYNTHESIS
HYDROGEN RECOVERY
MTG PROCESS
PRODUCT BLENDING
HEAVY GASOLINE HYDROTREATING

Fig. 1 – Coal-to-gasoline complex process flowsheet

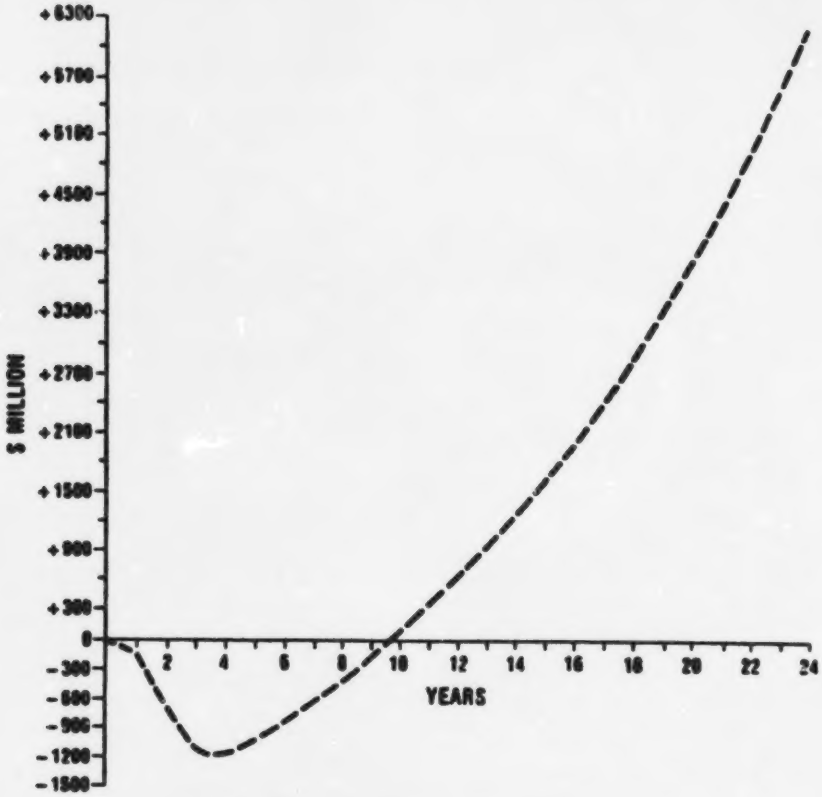

Fig. 2 – Economic analysis-cumulative net cash flow

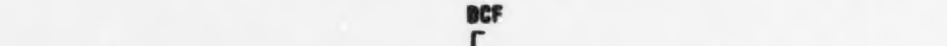

Fig. 3 – Economic analysis-base case sensitivities

SESSION IV

DISCUSSION

MODERATOR: B.I. PARSONS, CANMET

KELLY (CANMET): Mesba, what is the current status of the coal-to-gasoline project? It looks good on paper.

TAHERZADEH (PETRO-CANADA): Jim, as you know the project is proceeding to the second phase. However, Petro-Canada is not participating in the second phase. That was not my personal wish, of course, and there is another large oil company which has taken our position in this project. The project has proceeded based on the results of the first phase.

KELLY (CANMET): I really appreciated seeing those costs per daily barrel figures that you put up. I think they would be very handy to some of the people on the National Coal Conversion Coordinating Committee.

YAN (MOBIL): I have a slightly partisan view and I would like to make a comment on Mesba's nice presentation. I really liked your last slides too, particularly your conclusion. However, I would like to put forward a couple of other points in conjunction with this technology. I agree with all your premises but on the technology side we can be a little bit more optimistic. First of all, you are dealing with a very low-grade coal resource so the gasification part is very expensive. Thus we have to pay attention to the gasification side. All the economics can be improved considerably by improving the KT process. We have very good potential there. In fact, Mobil has tried to determine (with a gasifier company) what is the least-cost gasification process. Never mind the H_2/CO ratios, what is the best you can do? So we are in the process of developing a syngas conversion directly to methanol using very low hydrogen-to-carbon monoxide ratios. This is at a very good stage, not quite commercialized, but it is one of the projects which remains active, one of the very few projects that remains with the DOE technology.

I have a question for Norm Anderson. I recall that in your conclusions of phase one and phase two the conclusions seem to be reversed. Perhaps if I didn't make a mistake, I thought that in your first phase you showed that processing a lignite with methane gives you a little bit better economics, that is, the total product cost. When you turn around to the second phase, it seems to be the lignite alone that gives you a lower total product cost, including capital.

ANDERSON (KILBORN KELLOGG RUST): Okay, on those numbers there were some changes, particularly on the lignite plus natural gas option at low capital returns. In other words, if you looked at the numbers in particular where we had a 10% capital recovery, you did see a change. But if you looked at the numbers that were higher capital recovery of 15 and 20% there was no change. There was less of a difference maybe but the numbers still indicated that the lignite plus natural gas coprocessing option was slightly more attractive. We felt in the long term that the higher capital recovery factors were in fact more representative of what any industrial partner would demand to be involved in a project. I think the numbers that Mesba presented sort of confirmed that.

YAN (MOBIL): Excuse me. In your cost you have a capital recovery and beside this you did not include any DCF rate of return or did you?

ANDERSON (KILBORN KELLOGG RUST): That was not part of our work. That was done later I believe by the Ontario Energy Corporation using our information. We did not do a financial analysis.

YAN (MOBIL): If you do that, I think coprocessing will help you because your total capital is lower than the lignite alone. Is that correct?

ANDERSON (KILBORN KELLOGG RUST): Yes, the total capital per ton of methanol is lower in the coprocessing options. You see that in the higher capital recovery factors that we used in a lower product cost.

YAN (MOBIL): In other words, if you consider that in industry we have to make a few dollars, it will push you more to work with coprocessing.

ANDERSON (KILBORN KELLOGG RUST): Yes.

YAN (MOBIL): Speaking about this I have a question for Paul Watkinson. In almost your final slide you had a comparison of three processes, Westinghouse and so forth and yours. With respect to gas compositions, I thought those compositions were much more affected by the processing conditions, particularly temperature, steam ratio and so on. I did not see the way they were comparable in those three processes. How close are they toward equilibrium values of CO and hydrogen ratio? Are they close to equilibrium?

WATKINSON (UBC): As far as the first part of your question is concerned, I did have some figures on that transparency of the steam-to-oxygen ratios for the different processes. They were listed there and they are substantially different. As far as being near equilibrium, the answer is that at least the data from our gasifiers are fairly close to the water-gas shift equilibrium. There is some methane in there, so the equilibrium is a little more complicated than distance from the water-gas shift. They are fairly close to that, yes.

YAN (MOBIL): I would have thought that in most of the gasification processes under reasonable conditions, the compositions are very close to equilibrium, in many cases, or practically every case. If you are interested in changing the composition, you have to change the operation variables.

WATKINSON (UBC): Yes, I think that is true but you can't just simply change them without consideration of the heat balances and other things. For example, it's quite obvious that your equilibrium leaving a Lurgi gasifier at a relatively low temperature is clearly going to be different from that in a KT gasifier. I'm just trying to put some figures up there comparing some general numbers. I chose to compare them all with bituminous coals and we haven't obviously gasified our coals in the Lurgi.

We took the best numbers we could find from the literature. Some of the operating conditions were not given, we don't know what temperatures the Westinghouse gasifier was operating at and so it's just a general comparison in that sense. The coals are different in every case. The temperatures are different. The heat balances are different and so, as you say, the gas compositions are not strictly comparable in that sense.

PAPIC (BC HYDRO): I have a question for Norm Anderson. In your economic analysis of case three where you use electrolytic hydrogen for methanol production, I noticed you used a price of 2.7 cents per kWh. My question is, did you do any sensitivity analysis in which you would use only off-peak firm surplus power which would be obtained at much lower rates than at 27 mills per kWh?

ANDERSON (KILBORN KELLOGG RUST): We only looked at that in a very preliminary way because a financial or sensitivity analysis was not part of our work. We did do one case on electrolytic hydrogen where we looked at an electrical cost of 1.4 cents per kWh. It still showed the electrolytic hydrogen option to be the most expensive option. But again we did not do a lot of work there. That was not part of our contract.

TAHERZADEH (PETRO-CANADA): If I may interject and support Norm, we did look at this area at one point and we looked at the sensitivity of the cost of off-peak electric power. Due to the inefficiency of hydrogen production from electrolytic cells even if the price of electricity goes to zero, it still becomes more expensive than producing it from natural gas.

SHANNON (SHANNON and ASSOCIATES): It has been my observation that most analyses of electrolytic hydrogen are incorrect. They certainly were at the World Hydrogen Congress. That was agreed to by the Dean of Engineering at Caltech. Usually they just take the hydrogen off the electrolytic cell, and the hydrogen mole is slightly less stoichiometrically than the amount of oxygen. When you do that, you are actually charging an entire cell plus the operating conditions plus the full power train, against just the mole of hydrogen. If you take the oxygen which stoichiometrically is slightly more than the hydrogen and put it through a gasifier, you subsequently or consequently have reduced the capital cost of the electrolytic cells to half. The cost of the power train and the total cost of hydrogen drops to less than half. We did a study of this which unfortunately was given the odd time at the International Congress on Oil but nobody ever shows up at the meetings to look at electrolytic hydrogen and oil. As an example, at Lloydminster, the total cost of the electrolytic hydrogen and the power train was less than 10% of the total capital cost. It was an insignificant effect on the operation of a hydrogen addition type process. Furthermore, the steam reformer approach is sited as a very effective unit. The three units that are in operation in Alberta have never yet got through a winter as we all know. That was some of the down time that Mesba referred to. Electrolytic cells are reliable. I know one set that has been operating for over 30 years. I suggest that people review the new technical developments properly.

ANDERSON (KILBORN KELLOGG RUST): I think the only comment I want to make on that is in our study we did fully utilize the oxygen from the electrolytic cells as the oxygen supply for our gasifiers. So we did recognize that it was a necessary part of the overall processing scheme.

McELROY (BC RESEARCH): A question for Mr. Taherzadeh. What value, if any, did you put on the coal waste feed to your conversion plant? And if that value is non-zero, could you tell us what it was and then turn it over to Norm Anderson. Maybe he'd compare that to the value of the Onakawana feedstock at the plant?

TAHERZADEH (PETRO-CANADA): I'm sorry. This is one type of information which is kept fairly secret within the consortium. Westar Mining, the producer, does not want to publish the number. But it is fairly low. It's lower than what Norm mentioned about Ontario lignite. Of course I suppose you know that BC Hydro has looked at several different options or at several different times looked at different options.

MODERATOR (CANMET): In fairness, I think we do have to respect that in some of the studies where CANMET is a participant we are not the only participant and some aspects of the confidentiality period are still in effect. And Mesba and others do have a bit of a restraint.

SESSION V

COPROCESSING

Chairman: J.M. Denis

SESSION V: PAPER 18

COPROCESSING OF COAL AND HEAVY PETROLEUM CRUDES AND RESIDUA: A SOLVENT EVALUATION AND A PARAMETRIC STUDY

Christine W. Curtis, James A. Guin, Kan-Joe Tsai and Milo C. Pass

ABSTRACT

This study has investigated the combined hydroprocessing of coal with petroleum solvents consisting of heavy and reduced crudes and residua to determine the feasibility of simultaneous upgrading of both materials to lighter products. Six hydrogen-rich heavy petroleum materials have been processed with Illinois #6 coal at 400°C and 425°C for 30 minutes under three reaction conditions: a N_2 atmosphere, a H_2 atmosphere and a H_2 atmosphere using hydrotreating extrudates. Liquefaction of bituminous coal can be achieved in the petroleum solvents with coal conversion being dependent upon the reaction conditions. Noncatalytic coal conversions of 45 to 50% are achieved in a H_2 atmosphere. Addition of a catalyst increases conversion to near 70%. Only approximately 35% conversion is obtained in a N_2 atmosphere. In the catalytic environment substantial conversions to pentane soluble material occur. Individual differences in the abilities of petroleum solvents to solvate coal are observed from the product distributions obtained under noncatalytic conditions. Hydrotreatment and extraction of the solvent prior to coprocessing increase the amount of coal conversion and, in some cases, increase the amount of pentane soluble material produced. The influence of the solvent appears to be related to the molecular weight, viscosity and Conradson Carbon number of the petroleum materials.

Evaluation of the reaction parameters of temperature, hydrogen pressure, time and catalyst extrudate size for coprocessing has been undertaken. Based on the production of pentane soluble oil and coal conversion, feasible parameters are established: 425°C, 1250 psig H_2 pressure at ambient temperature, long reaction time and a hydrogenation catalyst with a small particle size. Combined processing is shown to be sensitive to catalyst extrudate size, with powdered catalyst giving substantially more oil yield and coal conversion than the extrudates.

PRÉSENTATION 18

COTRAITEMENT DU CHARBON ET DES BRUTS ET RÉSIDUS DE PÉTROLE LOURD: ÉVALUATION DES SOLVANTS ET ÉTUDE PARAMÉTRIQUE

Christine W. Curtis, James A. Guin, Kan-Joe Tsai et Milo C. Pass

RÉSUMÉ

Cette étude explore le cotraitement du charbon avec des bruts et des résidus de pétrole lourd réduits, en vue de déterminer si ces deux matières peuvent être valorisées simultanément. Six matières provenant de produits pétroliers riches en hydrogène ont été cotraitées avec du charbon de type Illinois n° 6 à 400 et 425°C durant 30 minutes dans trois conditions de réaction: une atmosphère N_2, une atmosphère H_2, et une atmosphère H_2 avec des extrudats catalyseurs d'hydrotraitement. La liquéfaction du charbon bitumineux peut s'effectuer dans les solvants de pétrole mais le taux de conversion du charbon dépend des conditions de réaction. Dans un environnement non catalytique et une atmosphère H_2, des taux de conversion de 45 à 50 % sont obtenus. L'addition d'un catalyseur augmente la conversion du charbon à près de 70 %. Dans une atmosphère de N_2, on obtient une conversion d'environ 35 % seulement. Dans l'environnement catalytique, des conversions importantes du charbon en matière soluble au penthane se produisent. Les différences individuelles au niveau de la capacité des solvants de pétrole à dissoudre le charbon sont observées, en se fondant sur les répartitions de produits générés par le traitement combiné dans des conditions non catalytiques. L'hydrotraitement et l'extraction du solvant avant le cotraitement augmentent la quantité de matière soluble au penthane obtenue grâce au cotraitement. L'influence du solvant semble être reliée à la masse moléculaire, à la viscosité et au résidu de carbone Conradson des matières pétrolières.

L'évaluation des paramètres de réaction applicables au cotraitement du charbon tels la température, la pression d'hydrogène, le temps de réaction et la taille des extrudats catalyseurs du cotraitement a été effectuée. Les paramètres obtenus en se basant sur la production d'huile soluble au pentane et sur le taux de conversion du charbon sont les suivants: une température de réaction de 425°C, une pression d'hydrogène initiale de 1250 psig H_2 à la température ambiante, un temps de réaction assez important, et un catalyseur d'hydrogénation ayant une brève course de diffusion. On a constaté que la course de diffusion constitue un facteur important du cotraitement. Les catalyseurs en poudre accroissent nettement la production de pétrole et la conversion du charbon.

COPROCESSING OF COAL AND HEAVY PETROLEUM CRUDES AND RESIDUA: A SOLVENT EVALUATION AND A PARAMETRIC STUDY

INTRODUCTION

The goal of coprocessing heavy petroleum crudes and residua with coal is to simultaneously upgrade both materials into higher quality liquid products. The benefits for coprocessing in terms of coal liquefaction are numerous. A primary benefit is that coprocessing offers a bridge between the present petroleum-based technology to a synthetic fuels coal-based technology. Additional benefits include the reduction of heteroatom content of both feeds and the boosting of the product octane rating due to the presence of the coal-derived synfuel.

The current investigation examines the feasibility of using heavy petroleum crudes and residua as solvents for bituminous coal. Previous work has centered on the use of bitumens (1,2) and individual residuum (3). This study extends previous investigations by offering a comprehensive examination of liquefaction and conversion of a bituminous coal in six different petroleum solvents and a typical coal-derived recycle solvent. The petroleum materials used encompass a wide range from whole to reduced crudes to a variety of residua. The simultaneous upgrading of both the coal and petroleum heavy ends is observed through comparison of the final product distribution to the original using a solubility separation technique. Chemical and physical characterizations of the petroleum materials have been performed to determine what factors are most influential in producing the end product slate.

The effects of reaction parameters for coprocessing of coal and heavy petroleum crudes and residua have been evaluated in this work. The primary parameters examined are the effect of reaction temperature, initial hydrogen pressure, reaction time, catalyst particle size, and catalyst loading. The basis for evaluation is the reaction product distribution obtained according to a solubility extraction scheme in which pentane solubles are defined as oil; benzene solubles, pentane insolubles as asphaltenes; methylene chloride/methanol solubles, benzene insolubles as pre-asphaltenes; and methylene chloride/methanol insolubles as insoluble organic matter or IOM. A schematic of the extraction scheme is given in Figure 1. In addition, the effects of catalytic treatment on the petroleum material and the effect of solvent pretreatment on coprocessing are also explored.

EVALUATION OF HEAVY PETROLEUM CRUDES AND RESIDUA AS COPROCESSING SOLVENTS

Six heavy petroleum crudes and residua have been used as solvents in a series of combined processing experiments. The experiments were performed at 400° and 425°C using a bituminous coal, Illinois #6, in three different environments: (1) an inert, N_2 atmosphere, (2) an H_2 atmosphere and (3) an H_2 atmosphere using presulfided $NiMo/Al_2O_3$ extrudates. The reactions were conducted in stainless steel tubing bomb reactors with typical volumes of $\sim 46\ cm^3$. In addition to the petroleum solvents, tetralin, and a coal-derived solvent, CPDU-200A, were used as bench marks. An elemental analysis of the coal used is given in Table 1 and the chemical and physical properties of the solvents are given in Tables 1 and 2.

Solvent extraction of Illinois #6 at ambient temperature yielded less than 10% soluble material in methylene chloride/methanol. When Illinois #6 coal was reacted in hydrogen without a solvent, ~35% of the coal was converted, primarily yielding preasphaltenes as the product. An equal, though small, amount, ~7%, of gas and oil was produced.

NONCATALYTIC PROCESSING IN AN INERT ATMOSPHERE

Combined processing experiments were performed in an inert, nitrogen atmosphere to determine how readily the hydrogen-rich petroleum solvents could transfer hydrogen directly to coal, thereby converting coal to a soluble product. The ability of the solvents to convert coal was measured directly by coal conversion to soluble products and gases. At 400°C and in nitrogen, the coal conversion to soluble products and gases obtained by using tetralin as the solvent was 57.3%; by CPDU-200A it was 51.5%; and the most converted by a petroleum crude was 36.0% (Table 3). The range of coal conversion in petroleum crudes and residua was from 28% to 36% as given in Figure 2. These data indicate that the petroleum crudes and residua do not contain much hydrogen readily donateable to coal. The proton distributions obtained from proton nuclear magnetic resonance (^{1}HNMR) substantiate this finding as will be described in a later section. Tetralin, by contrast, has hydrogens that are readily donable to coal and even in a hydrogen-deficient atmosphere is able to convert coal. The CPDU-200A is highly aromatic and contains both cyclic α and cyclic β hydrogens. The combination of these two factors provides for good physical solvation ability for coal as well as hydrogen donating ability.

A comparison of the oil yields from combined processing with the petroleum solvents is given in Figure 3. These yield values represent the weight per cent pentane soluble oil based on the total charge to the reactor. The original oil percentage at a constant solvent/coal ratio of 2:1 was variable due to the different oil contents of the respective solvents. An oil yield below the original value represents a decline in the pentane soluble fraction during the reaction. In the nitrogen atmosphere, tetralin was the only solvent that produced an increase in oil above that present in the original 2 to 1 solvent to coal mixture.

Compared to the original product distribution, the reaction products from combined processing using the petroleum solvents in a N_2 atmosphere were lower in pentane solubles. A general increase in the asphaltene content of the product liquids was observed as compared with the original charge. In the nitrogen environment, both the coal and the heavy petroleum materials may undergo polymerization, forming coke-like material which appears as IOM. In addition, the reacting coal may incorporate a significant portion of the petroleum soluble material into the coal matrix.

Two of the petroleum materials, Maya Crude and Lloydminster Reduced Crude, were used in experiments at all of the conditions listed in Table 3 (Fig. 4). The coal conversion in a N_2 atmosphere with Maya Crude is the same at 425°C as it is at 400°C. The coal conversion in Lloydminster Reduced Crude at 425°C was less than half the conversion at 400°C. The lowered conversion at 425°C indicates increased coking of the petroleum materials due to hydrogen deficiency.

NONCATALYTIC EXPERIMENTS WITH A HYDROGEN ATMOSPHERE

To eliminate some of the possible retrogressive reactions of the petroleum materials and the coal associated with the inert atmosphere, a hydrogen atmosphere was used in the combined processing. Tetralin converted the most coal, yielding 71.2%, while the coal-derived material CPDU-200A converted 56.8% (Fig. 2). Substantially more coal was converted in the hydrogen atmosphere with the petroleum solvents than in the nitrogen atmosphere. The coal conversion ranged from ~43% to 54% at 400°C depending upon the heavy petroleum crude or residuum used. The hydrogen atmosphere also either maintained or increased the oil yield as compared to the original charge in both the petroleum solvents and in CPDU-200A (Fig. 3).

Comparison of coal conversion at 400°C and 425°C in a hydrogen atmosphere in Maya Crude and Lloydminster Reduced Crude is shown in Figure 4. Coal conversion increases substantially with the 25°C temperature increase. With Maya Crude, the conversion incease is from ~50% to 62.5% and in Lloydminster Reduced Crude the increase is even greater, going from 49% to ~ 65%. In contrast, oil production is not strongly affected by the 25°C temperature increase. The increase in oil yield for Maya Crude is only 2% and for Lloydminster Reduced Crude, ~3.5%.

CATALYTIC COMBINED PROCESSING

Catalytic combined processing using presulfided Shell 324 NiMo/Al_2O_3 one-sixteenth extrudates has also been performed to determine the effect of a hydrotreating catalyst on coal conversion and the product distributions. For the petroleum heavy crudes and residua, the coal-derived CPDU-200A, and tetralin, the addition of presulfided NiMo/Al_2O_3 extrudates and reaction at 425°C in the presence of hydrogen increased both coal conversion and oil yield as shown in Figures 2 and 3, respectively. This increase is observed for reactions at both 400°C and 425°C when catalytic reactions are compared to noncatalytic. In those cases where the catalytic reactions were performed at both 400°C and 425°C, the primary effect in the increase in oil yields appears to be due to the presence of the catalyst. The oil yields from Maya Crude catalytic combined processing at 400°C are 69.2% and at 425°C, 72.3% compared to 59.9% and 62%, respectively, in noncatalytic processing (Fig. 4). Similar results are observed for Lloydminster Reduced Crude, 68.1% at 400°C and 71.5% at 425°C in catalytic processing compared to 58.8% and 62.2%, respectively, in noncatalytic processing.

CHEMICAL AND PHYSICAL PROPERTIES OF THE PETROLEUM HEAVY CRUDES AND RESIDUA

Among the six petroleum materials used in this study, individual differences are apparent in their ability to convert coal and produce pentane soluble materials. The chemical and physical properties of the petroleum materials are different and may influence their performance in coprocessing. As the viscosity of the petroleum crudes and residua increases, the specific gravity increases and the °API gravity decreases. A general increase in Conradson Carbon residue and refractive index is also observed. The number average molecular weight for most of the petroleum solvents also increases with viscosity, with the exception of Lloydminster Reduced Crude.

From these analyses, some general comments can be made concerning the properties of the petroleum solvents. Each petroleum heavy crude and residua is composed primarily of pentane soluble material although each contains large asphaltenic compounds, as evidenced by a ~6 to ~20% lack of solubility in pentane and a corresponding solubility in benzene. All of the petroleum solvents are hydrogen-rich, high in sulphur and have nitrogen values between 0.20 to 0.50%. The coal-derived solvent has higher oxygen and nitrogen content and much lower sulphur. The typical hydrogen-to-carbon ratio for coal-derived liquids is 1.0 or less; all of the petroleum crudes and residua used in this study have H/C ratios in the range of 1.45 to 1.65. The ash levels in the petroleum crudes range from 0.012 wt % for West Texas VSR to 0.082 wt % for Mayan TLR.

Proton distributions of the petroleum solvents indicate that all of the petroleum solvents are highly aliphatic. Proton NMR analysis shows the protons present to be primarily alkyl β and γ protons. Fewer hydroaromatic protons, cyclic α and cyclic β protons are present. Calculation of the fraction aromatic, f_a, from structural group analysis yields f_a values ranging from 0.32 to 0.37. In contrast, the coal-derived CPDU-200A solvent is quite aromatic with an f_a value of 0.70. Comparing the proton distribution of CPDU-200A to the petroleum solvents reveals that CPDU-200A contains many more condensed aromatic and hydroxl protons than do the petroleum materials. In terms of aliphatic protons, CPDU-200A has a higher percentage of cyclic α and alkyl α protons and less cyclic β, alkyl β and γ protons than do the petroleum materials. Infrared analysis shows that the aromatic C-H to aliphatic C-H_2 stretch ratios are almost an order of magnitude less for the petroleum solvents than for the CPDU-200A. These data indicate that the petroleum solvents are highly aliphatic whereas the coal-derived CPDU-200A solvent is much more aromatic. The ratio of methyl groups to methylene groups is higher in the petroleum solvents than in CPDU-200A. More methyl groups may indicate the presence of more end groups on aliphatic chains in the petroleum solvents compared to methylene groups in naphthenic ring structures, as part of hydroaromatic compounds, for example in the coal-derived solvent.

Taking all of the above into consideration, the petroleum resids used in this study would be predicted to be poorer solvents for coal liquefaction than CPDU-200A since they have less donable hydrogen, lower aromaticity, higher saturated carbon content, and higher coking potential.

RELATIONSHIP BETWEEN SOLVENT PROPERTIES WITH COAL CONVERSION

Coal conversion in the petroleum solvents using a hydrogen atmosphere at 400°C appeared to be related to the viscosity, molecular weight and Conradson Carbon number of the petroleum materials (Table 4). Coal conversion does not follow the aromaticity or the amount of asphaltenes present in the different petroleum crudes and residua. The highly viscous solvents, Kuwait resid and West Texas VSR, give less coal conversion than do the less viscous petroleum solvents. The petroleum solvents with lower Conradson Carbon numbers give higher coal conversion. The difference in apparent coal conversion may result from increased coking of the petroleum residua having high Conradson Carbon numbers. Hydrogenation experiments have been performed using Maya Crude and West Texas VSR with no coal present to observe the effect on the product distributions. Maya Crude reacted quite differently from West Texas VSR. For Maya Crude, the asphaltene level was decreased by one-third; the new products formed were gas, preasphaltenes and IOM. In contrast, after reaction, the West Texas VSR lost oil, gained a small amount of asphaltenes and produced the same new products as did Maya Crude. The amount of IOM produced, 2.3%, was greater for West Texas VSR than for Maya Crude, 0.8%. The IOM amounts agree with the Conradson Carbon numbers for the two materials. The effect of processing in H_2 on West Texas VSR will most likely be reflected in the coprocessing reactions with coal.

A similar trend on the effect of coal conversion is observed with molecular weight. The petroleum solvents with lower molecular weights, Lloydminster Reduced Crude, West Texas TLR, Maya Crude and Maya TLR, show increased coal conversion. West Texas TLR, which has the lowest Conradson Carbon and the second-lowest molecular weight and viscosity, gives the highest coal conversion of any of the petroleum solvents during coprocessing. In general, the higher the viscosity of the crude, the lower the coal conversion obtained during liquefaction.

The addition of a catalyst changes the order of the coal conversion among the six petroleum solvents and apparently the relative importance of the solvents' properties. No obvious correlations exist between the above-mentioned solvent properties and coal conversion when a catalyst is used.

PARAMETRIC EVALUATION

The effect of reaction conditions on combined coal and heavy crude or residuum processing has been evaluated for the parameters of reaction temperature, initial hydrogen pressure, reaction time and diffusional path length of the catalyst. For these studies, Maya Crude was used as the solvent. In addition, the effect of catalyst loading and solvent pretreatment has been examined using untreated and hydrotreated residua. Two coals were used, Illinois #6 and Clovis Point, with Illinois #6 coal being used for the majority of the experiments. When reacted at 425°C in hydrogen, in the absence of a solvent and catalyst, ~35% of Illinois #6 was converted and ~46% of Clovis Point. At 425°C and in the presence of H_2, Maya Crude, which originally contained 85% oil and 15% asphaltenes, was thermally reacted. No substantial change in the Maya Crude product distribution occurred. Upon catalytic hydrogenation using a powdered hydrogenation catalyst, a 4% increase in oil was observed along with an increase in gas production. In all cases the asphaltene content was reduced, the greatest reduction being obtained in the presence of the catalyst.

EFFECT OF TEMPERATURE ON THE PRODUCT DISTRIBUTION FROM ILLINOIS #6 WITH MAYA CRUDE

The effect of reaction temperature on the product distributions from combined processing was examined by reacting Illinois #6 and Blacksville Mine coals in Maya Crude at temperatures ranging from 375°C to 475°C at 25 degree intervals. The product distributions from these reactions using Illinois #6 coal are shown in Figure 5. With increasing temperatures, higher oil yields and increased coal conversions were observed as the reaction temperature increased from 375°C to 425°C. A maximum in oil yield and a minimum in IOM occurred at 425°C. At temperatures above 425°C, high gas yield and increased IOM yields are observed. The increased IOM yields may result from production of methylene chloride/methanol insolubles from the petroleum solvent as well as from the coal.

EFFECT OF INITIAL HYDROGEN PRESSURE ON COMBINED PROCESSING

The sensitivity of combined processing to initial hydrogen pressure has been evaluated by increasing the initial hydrogen pressure measured at ambient temperature from 0 to 1500 psig. The reactions were performed for 30 minutes at 425°C using Illinois #6 coal, Maya Crude and a powdered, presulfided NiMo/Al_2O_3 hydrogenation catalyst to increase efficiency of hydrogen utilization. The product distributions obtained from these reactions shown in Figure 6 clearly demonstrate that the absence of a hydrogen atmosphere results in the production of a large amount of IOM, giving an apparent coal conversion of only 8.6%. Comparing this conversion to that of thermally reacted coal with no solvent in a hydrogen atmosphere, the hydrogen atmosphere increases coal conversion by more than 20%. In a hydrogen-deficient atmosphere, the petroleum solvent may also be undergoing retrogressive reactions forming coke-like materials adding to the IOM. The production of material insoluble in methylene chloride/methanol has been observed when Maya Crude is reacted by itself at combined processing conditions in a N_2 atmosphere. At an initial hydrogen pressure of 250 psig, the pentane soluble oil yield was higher than that in the original mixture; coal conversion was 52.5%. Thus, even low levels of hydrogen can be effective in reducing the number of retrogressive reactions occurring when solvent and catalyst are present to aid in the transfer of hydrogen to coal. A hydrogen atmosphere appears also to be necessary to eliminate some of the retrogressive coking-type reactions of the solvent. As the hydrogen pressure was increased, coal conversion climbed, yielding 86.9% at 1500 psig. The oil produced also increased, yielding 78.5% at 1500 psig. Above 500 psig, the rate of increase for both coal conversion and pentane soluble yields was lower than between 0 and 500 psig.

EFFECT OF TIME AND CATALYST DIFFUSION PATH LENGTH ON PRODUCT DISTRIBUTIONS FROM THE COMBINED PROCESSING OF ILLINOIS #6 COAL

Two parameters were studied simultaneously in the next series of experiments: reaction time and the effect of catalyst diffusion path length. Previous work has shown that the length of the diffusion path, which a molecule must travel during hydroprocessing to reach an active catalytic site, has a definite effect on the products obtained during the reaction (4,5). To determine the effect of time and diffusion path length on combined processing, three sets of experiments using Illinois #6 in Maya Crude were performed: (1) thermal reaction with no catalyst present, (2) reactions with presulfided NiMo/Al_2O_3 catalyst pellets, and (3) reactions with presulfided NiMo/Al_2O_3 powdered catalysts. The reaction times studied were 7.5, 15, 30, 45, 60 and 90 minutes. For all three reaction conditions, coal conversion increased with increasing reaction times up to 45 minutes, as shown in Figure 7. After then, coal conversion did not increase substantially and appeared to level out for all three conditions. The presence of a catalyst increased the amount of coal conversion when compared to the thermal experiments. The pelleted catalyst increased coal conversion slightly, while the powdered catalyst increased the amount of coal conversion substantially.

From these experiments, it is apparent that the longer residence time the coal has in a hydrogen atmosphere the more coal will be converted. The use of a catalyst increases the availability of the hydrogen to the coal and increases the rate of coal dissolution. The presence of a powdered catalyst makes hydrogen more available to the coal by providing increased contact between the catalyst active sites and the dissolving coal matrix. This increased availability results from a decrease in the diffusional path length required for the coal molecules to traverse before coming into contact with an active site.

Hydrogen consumption in the thermal and in both catalytic experiments increased with increasing time. The coprocessing experiments using the powdered catalyst consumed more hydrogen than did either the experiments using pellets or no catalyst. The hydrogen consumption data correlate with the yields of pentane solubles produced under the three conditions as presented in Figure 8. The order of pentane solubles produced in these three experiments were: powdered > pellet > thermal. The data, presented in Figure 8, shows the oil production from the three cases as a percentage of the upgradable material present initially in the reactor. The upgradable material is defined as the sum of the maf coal and petroleum asphaltenes present at the beginning of the reaction. The catalyst obviously aids in oil production, with the powdered form yielding significantly greater oil production than the extrudates. These data are a clear indication of the influence of pore diffusional restrictions in limiting the oil yield with extrudates. The shorter the diffusional path length in combined processing, the more likely a potentially upgradable moiety will contact the catalytic surface.

COMBINED PROCESSING USING A SUBBITUMINOUS COAL

A Clovis Point subbituminous coal from Wyoming has also been evaluated in thermal and catalytic combined processing. The reaction conditions for this evaluation were 30 minutes reaction time, Maya Crude as the solvent, using no catalyst, catalyst extrudates and powdered catalyst. The product distributions obtained from these reactions show trends similar to those obtained from Illinois #6 coal. Both oil production and coal conversion increased with catalytic treatment, the highest yields being produced from the powdered catalyst. For comparable reaction times, coal conversion from Clovis Point coal was slightly higher than Illinois #6 for the thermal and pelletized catalyst cases, but not when the catalyst was powdered. Oil production from Clovis Point coal was consistently 5 to 6% higher than Illinois #6 coal for all reaction conditions.

EFFECT OF CATALYST LOADING ON COPROCESSING

The effect of catalyst loading on the product slate from coprocessing using original untreated West Texas VSR (Fig. 9) and hydrotreated West Texas VSR has been evaluated. For both solvents, as the catalyst loading is increased from 0 to 33% of the total charge, the oil yield steadily increases while the preasphaltene level steadily decreases. The asphaltene fraction begins to decrease when the catalyst loading is 11.1% of the total charge. For the untreated residuum, coal conversion appears to reach a maximum between 2.8% and 11.1% catalyst loading, and then declines with increased catalyst loading. For the hydrotreated solvent, coal conversion within the thermal reaction is high, 83%, and no maxima is observed in the coal conversion versus catalyst loading curve; at high catalyst loadings the decline in coal conversion is still observed. The reasons for the maxima and for the subsequent decline in coal conversion are unclear and may be a combination of several factors. Catalytic pretreatment of the solvent appears to remove the coke-producing compounds and yields a superior solvent for coal conversion, thereby removing the maxima in coal conversion. The decrease in coal conversion at high-catalyst loadings may in part be due to an inventory buildup of material within the catalyst pores. The change in coal conversion would be apparent in a batch reactor system such as used in this study, although it would not be apparent in other reactor systems. Another possible explanation for the decrease in coal conversion may be the deposition of insoluble material on the catalyst surface resulting from hydrocracking reactions in which oil is obtained from asphaltenes and preasphaltenes.

EFFECT OF SOLVENT PRETREATMENT ON COPROCESSING

Catalytic hydrotreatment of the heavy petroleum crudes and residua upgrades a portion of the material to oil while some gas, preasphaltenes and IOM are formed. Since the petroleum heavy ends change in composition and character upon hydrotreatment, pretreating the solvent followed by extracting with a solvent to remove any insolubles generated may produce a superior solvent for coprocessing. The effect of pretreatment of West Texas VSR in noncatalytic and catalytic coprocessing has been examined in terms of oil yields and coal conversion (Fig. 10 and 11). Pretreatment of West Texas VSR involved hydrotreatment at 380°C using a $NiMo/Al_2O_3$ catalyst in oxide form and at 425°C using presulfided $NiMo/Al_2O_3$, followed by extraction with THF. When these pretreated solvents were used in noncatalytic coprocessing, a substantial increase in coal conversion and a small increase in oil yield are observed. In catalytic coprocessing coal conversion was slightly higher in the hydrotreated solvent than in the untreated solvent. The oil production from catalytic processing using untreated and hydrotreated West Texas VSR was nearly the same, 33.1% and 31.7%, respectively. The effect of solvent pretreatment on oil production appears, however, to be dependent upon the petroleum material used. Similar experiments using Maya TLR showed a substantial increase in oil production, 49.6%, using the hydrotreated residuum compared to 32.8% using the untreated residuum.

A second pretreatment in which pentane was used to remove the asphaltenes from West Texas VSR was examined. In some cases, the pentane fraction was catalytically hydrotreated with presulfided $NiMo/Al_2O_3$ and then extracted with THF prior to being used as a coprocessing solvent. In the thermal reactions, coal conversion was highest in hydrotreated pentane-extracted West Texas VSR. The highest coal conversion in the coprocessing reactions using West Texas VSR was achieved in a catalytic reaction using hydrotreated pentane-extracted West Texas VSR.

SUMMARY AND CONCLUSIONS

Petroleum crudes and residua and coal have been coprocessed at typical liquefaction conditions in atmospheres of nitrogen and hydrogen and in the presence of hydrogen and a catalyst. At 400°C coal conversion in a nitrogen atmosphere was low and at the same level as the thermal coal reaction with no solvent, indicating that little transfer of hydrogen from the petroleum solvents to the coal occurred. Coal conversion increased in the presence of hydrogen; further increases in coal conversion were observed in the presence of catalyst at 400°C and 425°C. Both an increase of temperature of 25°C and the presence of a hydrotreating catalyst at a given reaction temperature have a substantial effect on coal conversion. The catalytic treatment has the larger effect. Oil production from combined processing showed negative or level yields in the N_2 atmosphere, level or slightly positive yields in the H_2 atmosphere and for most petroleum solvents significant increases when a catalyst and hydrogen were both present. As in the case of coal conversion, the presence of a catalyst appears to be the dominant factor with the increase in temperature having a secondary effect.

Individual differences among the petroleum solvents are observed in the product distributions obtained from combined processing. Coal conversion in the H_2 atmosphere appears to be related to viscosity, molecular weight and Conradson Carbon number of the petroleum crude. The Conradson Carbon number is directly reflected in the amount of IOM produced from the petroleum solvent and results in a lowered apparent coal conversion. These particular solvent characteristics do not seem as important in coal conversion when a catalyst is present.

The parametric evaluation has shown that feasible conditions for combined processing are:

Reaction Temperature:	425°C
Hydrogen Pressure:	above 500 psig initial hydrogen pressure
Time:	90 minutes
Catalyst:	minimum particle size

Combined processing of coal and a petroleum solvent is sensitive to the diffusional path length of a catalyst and appears to be more sensitive than the liquefaction of coal in a coal-derived solvent (6). The use of hydrotreated solvent coprocessing increases the amount of coal conversion obtained and in some cases the amount of oil production.

Combined processing adds greater flexibility to the liquefaction of coal by eliminating the need for solvent sufficiency and for large recycle streams. Additionally, coprocessing provides an avenue by which difficult to refine heavy petroleum crudes and residua with large asphaltene contents can be upgraded. Combined processing should be considered as a transitional concept leading to the coal liquefaction processing plants of the future while utilizing and upgrading difficult to refine heavy petroleum materials of today.

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TABLES

Table 1 – Analysis of solvents and coals used in coprocessing

Solvents and coal	Product distribution (wt %)				Ash, wt %	Elemental analysis					
	Oil	Asphaltenes	Pre-asphaltenes	IOM		C	H	N	S	O by difference	H/C
Maya crude (sample "C")	84.4	15.6			0.058	84.6	11.5	0.36	3.09		1.63
West Texas TLR (sample "B") (82% West Texas, 8% Alaskan N.S., 5% Isthmus, 5% Seripano Terra)	93.6	6.4			0.033	86.4	11.0	0.34	2.80		1.51
Mayan TLR (sample "C")	79.5	20.5			0.082	85.3	10.8	0.51	4.19		1.51
Lloydminster reduced crude	84.0	16.0			0.039	85.0	10.7	0.34	4.35		1.49
Kuwait resid	88.96	10.99	0.05		0.031	79.5	10.3	0.19	4.63		1.55
West Texas Vacuum Short resid (sample "E-201")	88.7	11.3			0.012	86.1	10.4	0.44	3.33		1.47
CPDU-200A	85.48	12.47	1.16	0.89		89.3	7.3	1.20	0.56		0.97
Illinois #6					10.6	68.4	4.4	1.4	3.2	12.0	
Clovis Point					9.0	65.4	5.0	0.9	1.0	18.7	

Table 2 – Chemical and physical properties of the petroleum heavy crudes and residua solvents

Solvents	Molecular weight	fa	$\overset{20}{D}$	Viscosity (poise) 40°C	Specific gravity 60°F/60°F	°API	Conradson carbon residue
Maya crude	577	0.32	1.52	0.924	0.920	22.3	10.41
West Texas TLR	545	0.35	1.55	28.2	0.979	13.0	10.34
Mayan TLR	668	0.37	1.56	317	1.000	10.0	15.87
Lloydminster reduced crude	481	0.36	1.57	389	1.004	9.44	14.23
Kuwait resid	961	0.34	1.58	3470	1.014	8.05	17.00
West Texas VSR	922	0.35	1.58	7075	1.014	8.05	17.33
CPDU-200A	205	0.70					

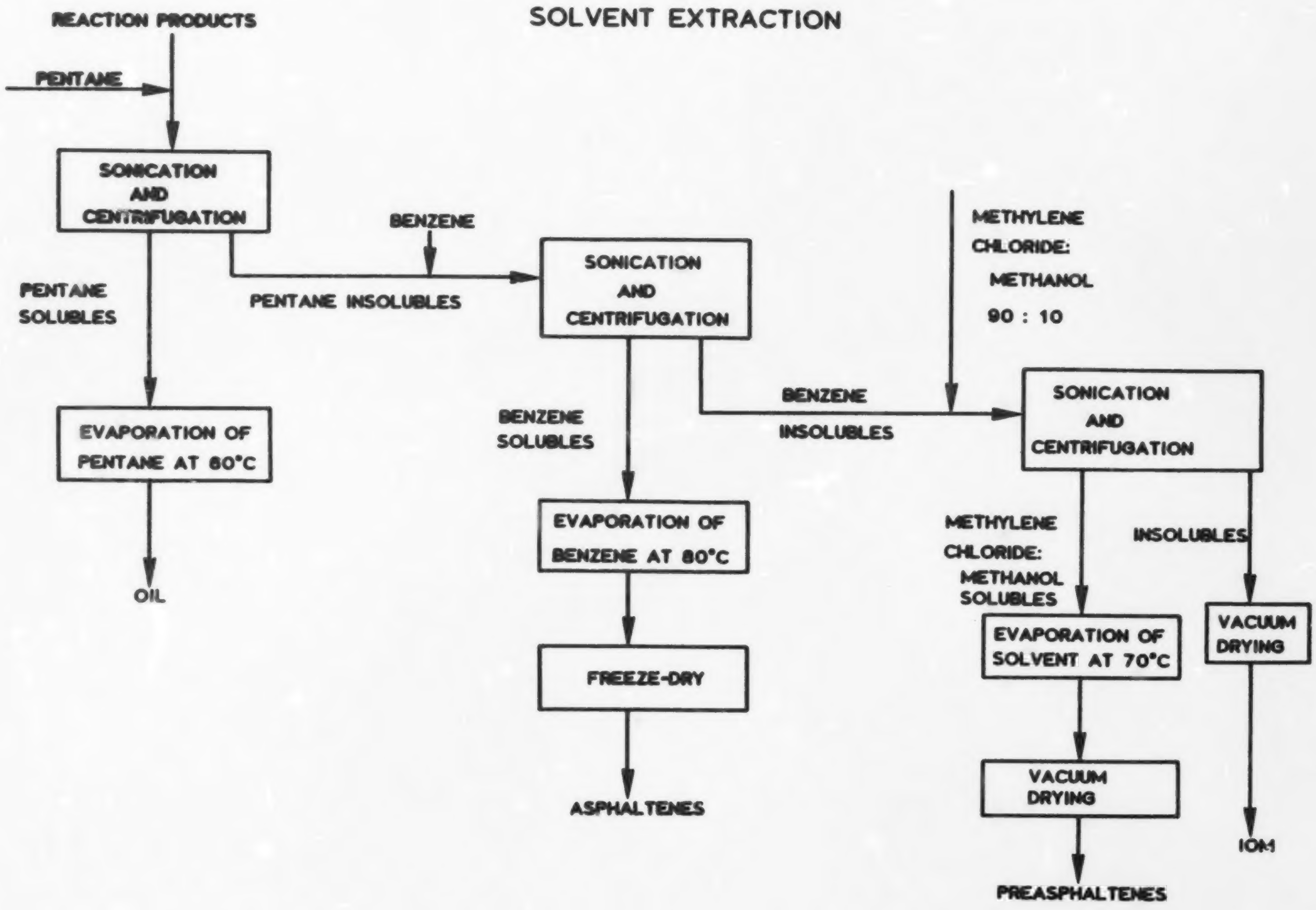
Table 3 – Effect of atmosphere and catalyst on oil production and coal conversion

Oil, wt %	Tetralin	Maya crude	West Texas TLR	Mayan TLR	Lloydminster reduced crude	Kuwait resid	West Texas VSR	CPDU 200A
Original	67.5	56.9	63.2	53.7	56.7	60.0	59.8	57.7
N_2, 400°C	70.6	58.7	60.4	53.2	55.7	56.0	54.0	53.4
H_2, 400°C	71.2	59.9	65.8	56.4	58.8	60.4	58.4	56.3
H_2 + $NiMo/Al_2O_3$, 400°C		69.2			68.1		64.0	
N_2, 425°C		58.2			51.5			
H_2, 425°C		62.0	65.1		62.2		58.1	
H_2, $NiMo/Al_2O_3$, 425°C	83.1	72.3	73.7	66.3	71.5	68.2	66.9	73.8
Average conversion, %								
N_2, 400°C	57.2	28.4	30.2	34.9	28.4	30.2	26.7	50.3
H_2, 400°C	70.6	49.8	53.5	49.3	48.9	45.2	44.5	56.6
H_2, $NiMo/Al_2O_3$, 400°C		67.3			72.1		52.9	
N_2, 425°C		28.9			13.2			
H_2, 425°C		62.5			64.7		58.5	
H_2 + $NiMo/Al_2O_3$, 425°C	81.0	66.2	68.9	62.3	75.2	69.2	65.4	81.6

Table 4 – Comparison of coal conversion with properties of the petroleum solvents

Petroleum crudes and resids	Coal conversion, %	Viscosity (Poise) 40°C, 300 mm Hg	Conradson carbon residue	Molecular weight
Maya crude	49.8	0.932	10.41	577
West Texas TLR	53.5	28.2	10.34	545
Mayan TLR	49.3	317	15.87	668
Lloydminster reduced crude	48.9	389	14.23	481
Kuwait resid	45.2	3470	17.00	961
West Texas VSR	44.5	7075	17.33	922

FIGURES


SOLVENT EXTRACTION

REACTION PRODUCTS
PENTANE
SONICATION AND CENTRIFUGATION
PENTANE SOLUBLES
EVAPORATION OF PENTANE AT 60°C
OIL
PENTANE INSOLUBLES
BENZENE
SONICATION AND CENTRIFUGATION
BENZENE SOLUBLES
EVAPORATION OF BENZENE AT 80°C
FREEZE-DRY
ASPHALTENES
BENZENE INSOLUBLES
METHYLENE CHLORIDE: METHANOL 90 : 10
SONICATION AND CENTRIFUGATION
METHYLENE CHLORIDE: METHANOL SOLUBLES
EVAPORATION OF SOLVENT AT 70°C
VACUUM DRYING
PREASPHALTENES
INSOLUBLES
VACUUM DRYING
IOM

Fig. 1 – Solvent extraction scheme used for reaction products from combined processing

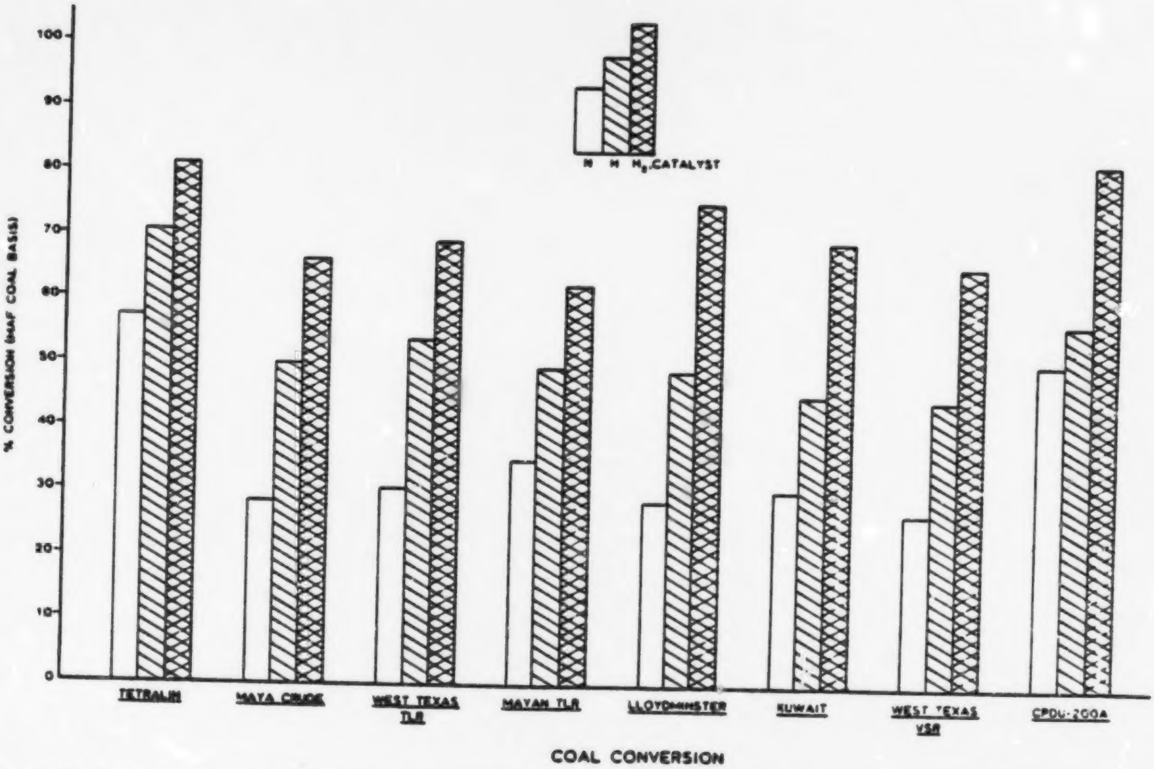


Fig. 2 – Coal conversion obtained from combined processing using environments of N_2, H_2, and H_2 plus a catalyst

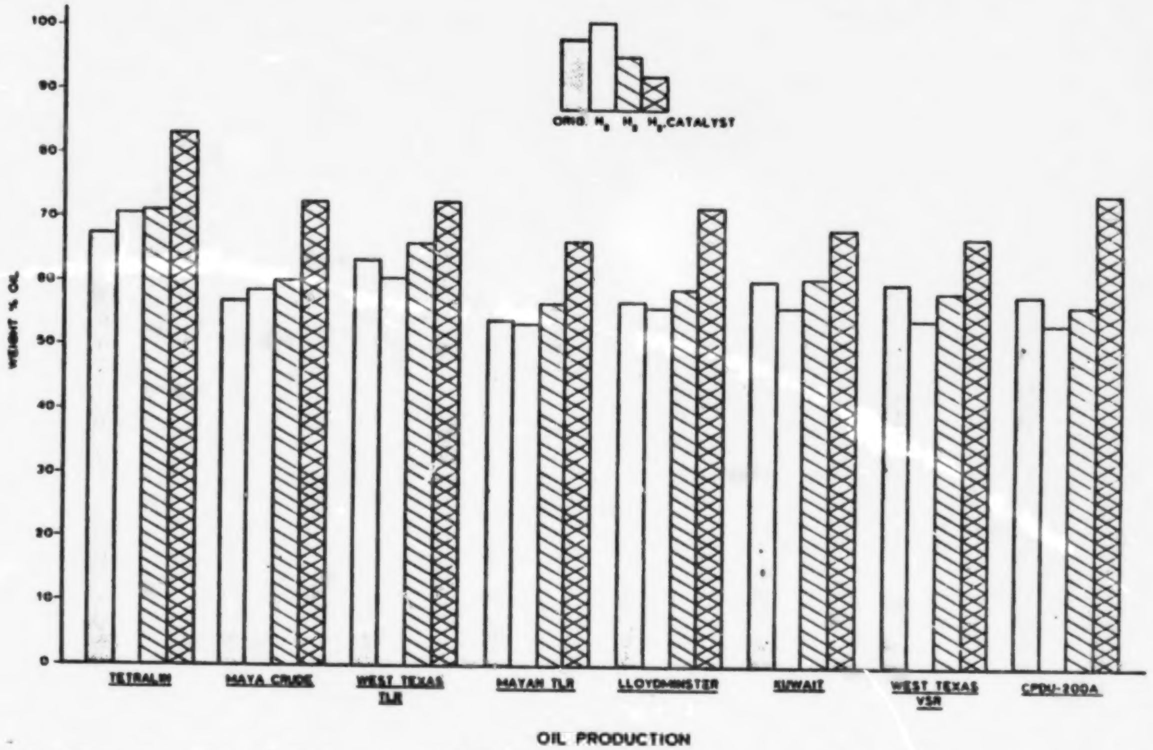


Fig. 3 – Comparison of oil yields from combined processing using environments of N_2, H_2, and H_2 plus a catalyst

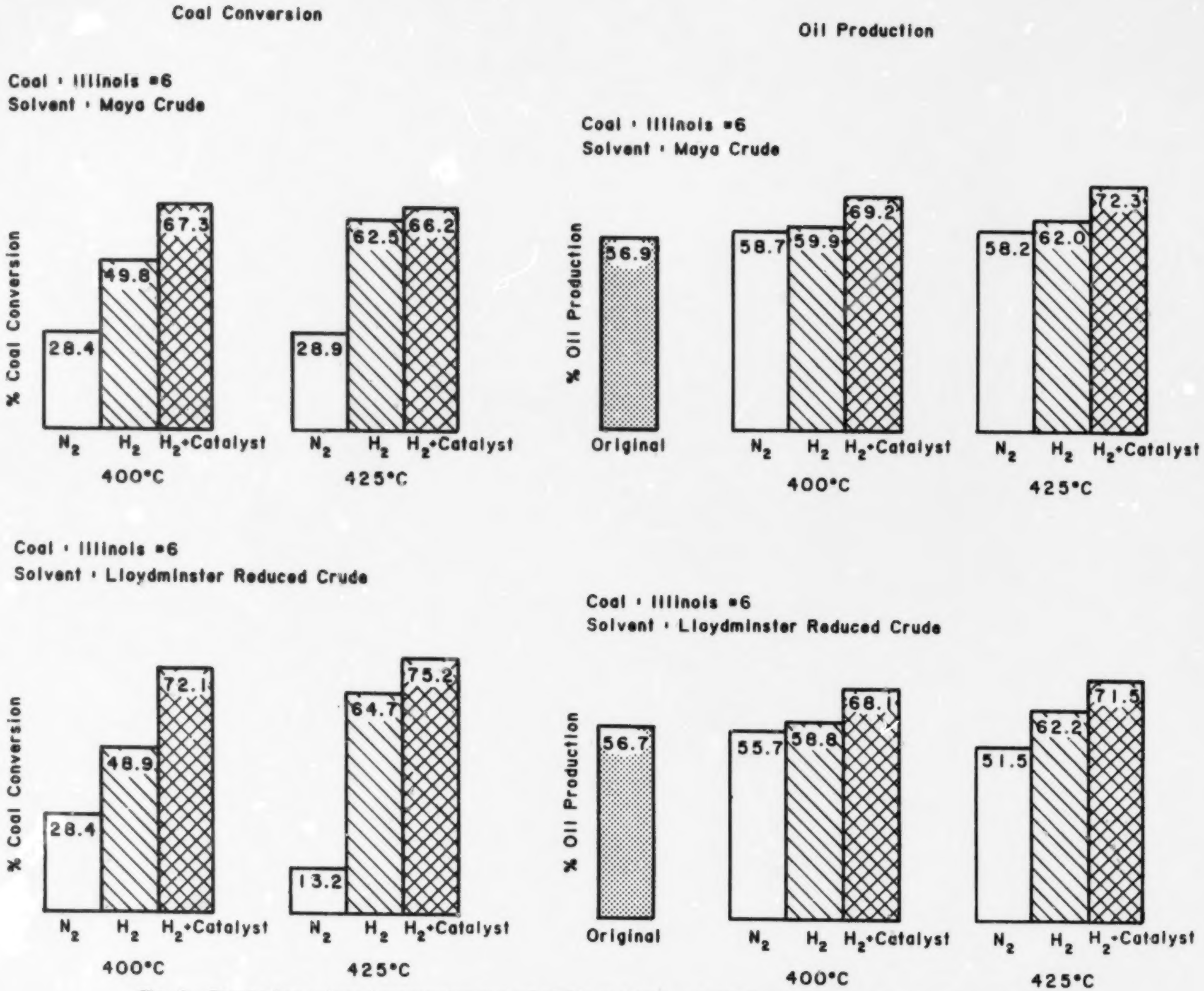


Fig. 4 – Comparison of coal conversion and oil yields at 400°C and 425°C using Maya Crude and Lloydminster Reduced Crude in coprocessing

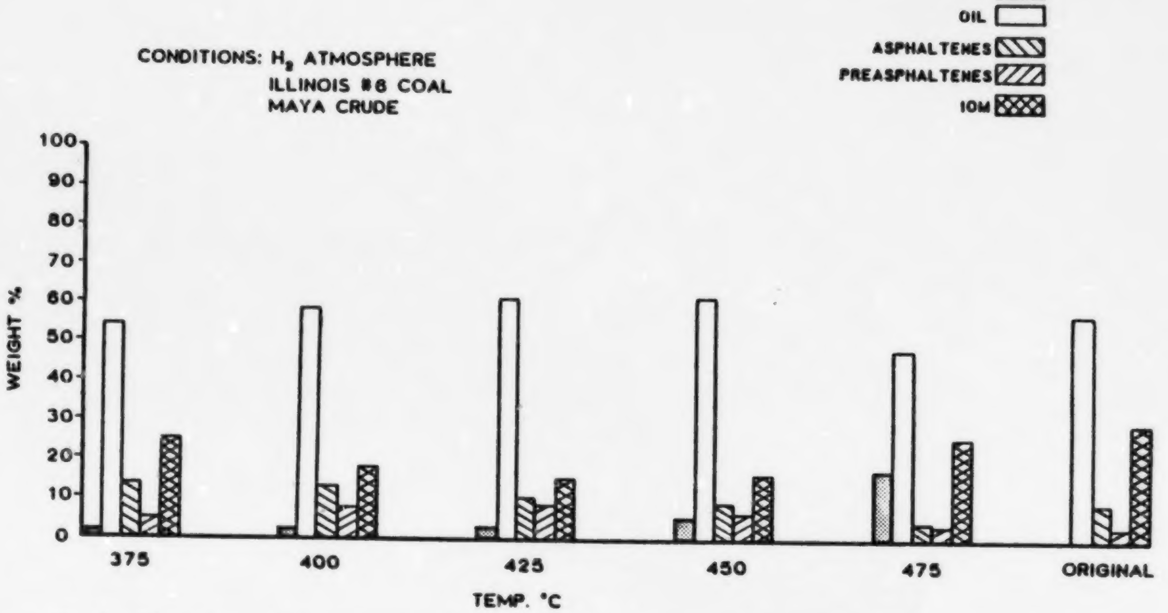


Fig. 5 – Effect of reaction temperature on the combined processing of Illinois #6 coal and Maya Crude

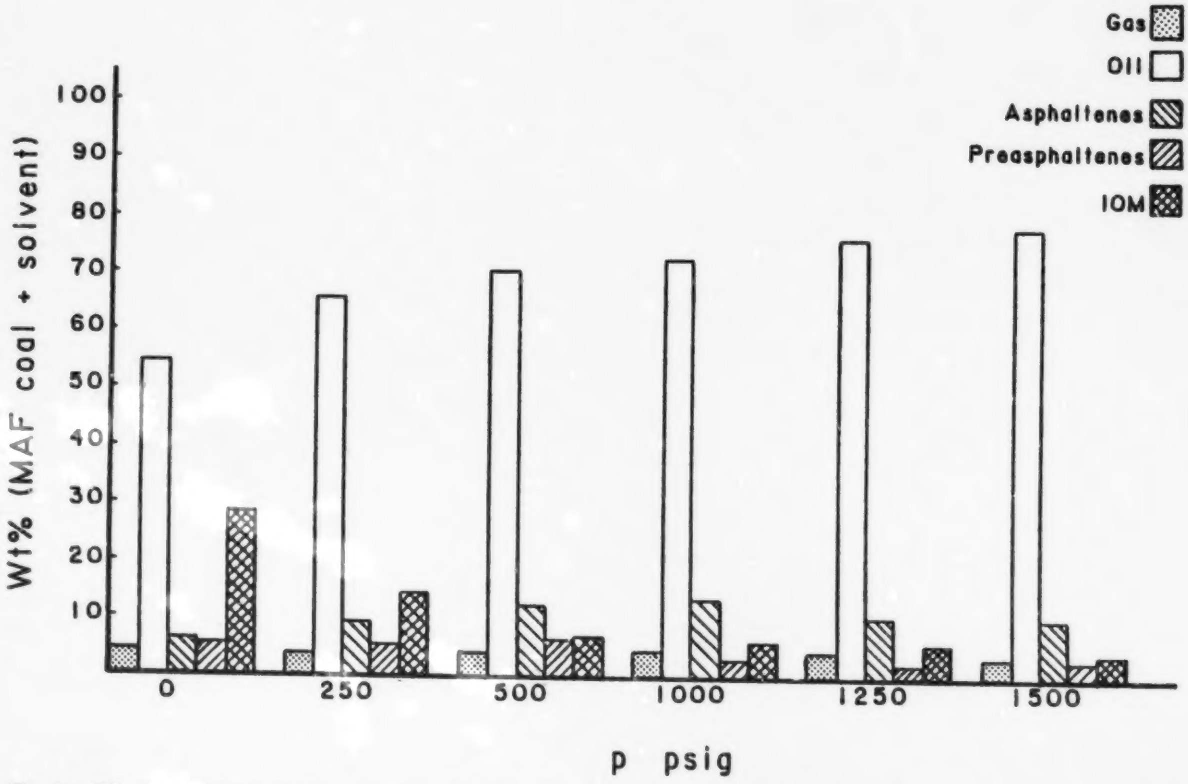


Fig. 6 – Effect of initial hydrogen pressure on the products from coprocessing of Illinois #6 coal and Maya crude

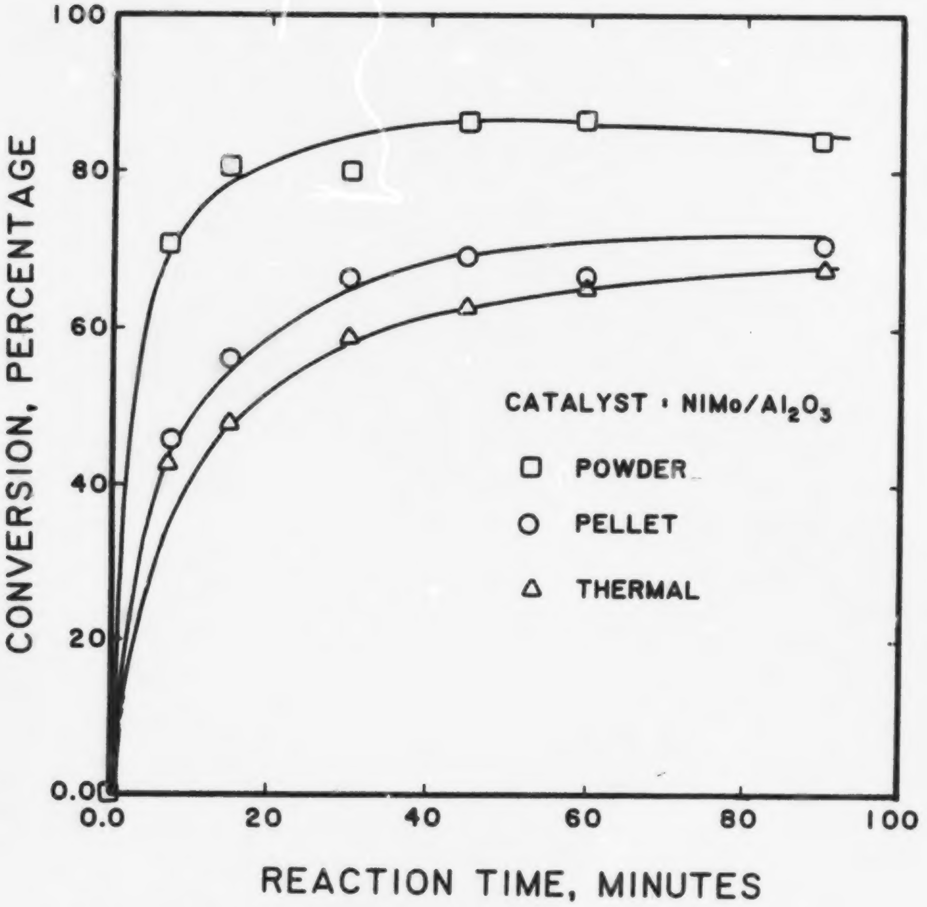


Fig. 7 – Effect of reaction time and catalyst particle size on coal conversion

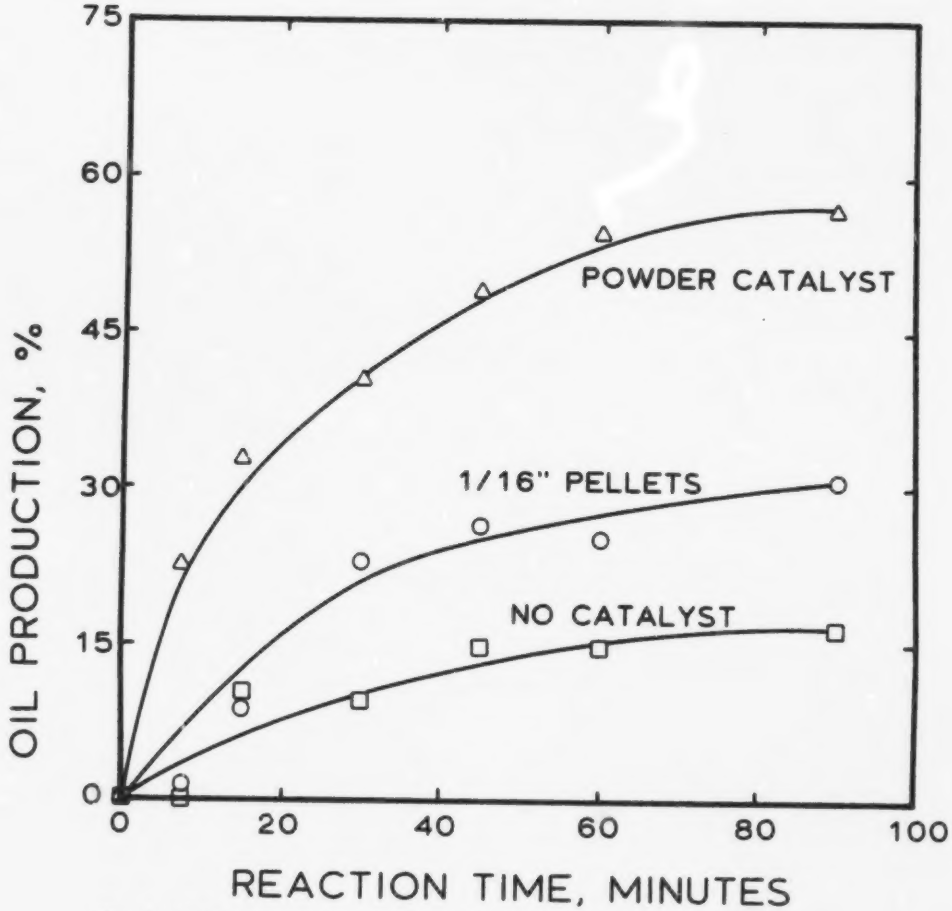


Fig. 8 – Effect of reaction time and catalyst particle size on oil production

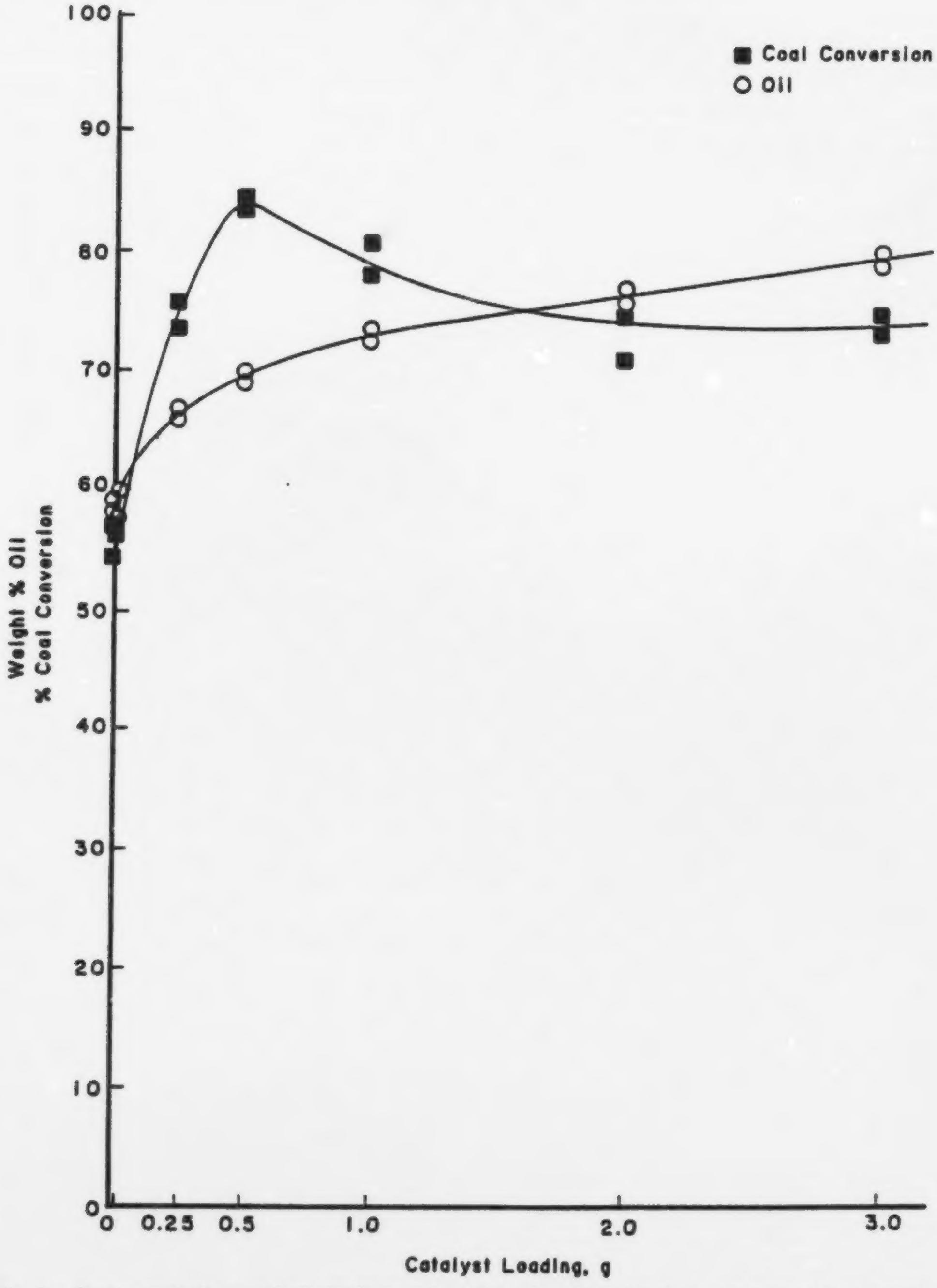


Fig. 9 – Coal conversion and oil yields as a function of catalyst loading using West Texas VSR

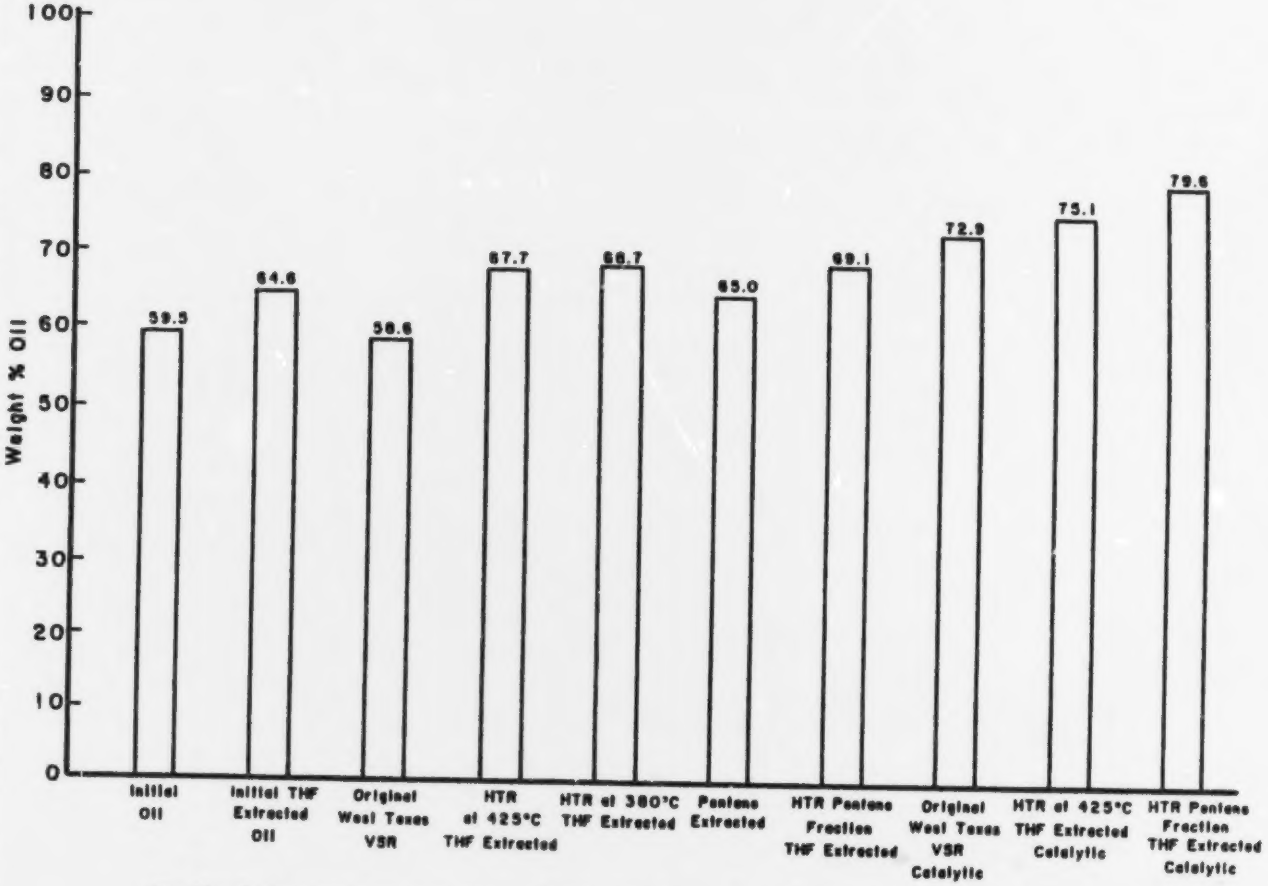


Fig.10 – Coal conversion from thermal and catalytic reactions using pretreated West Texas VSR

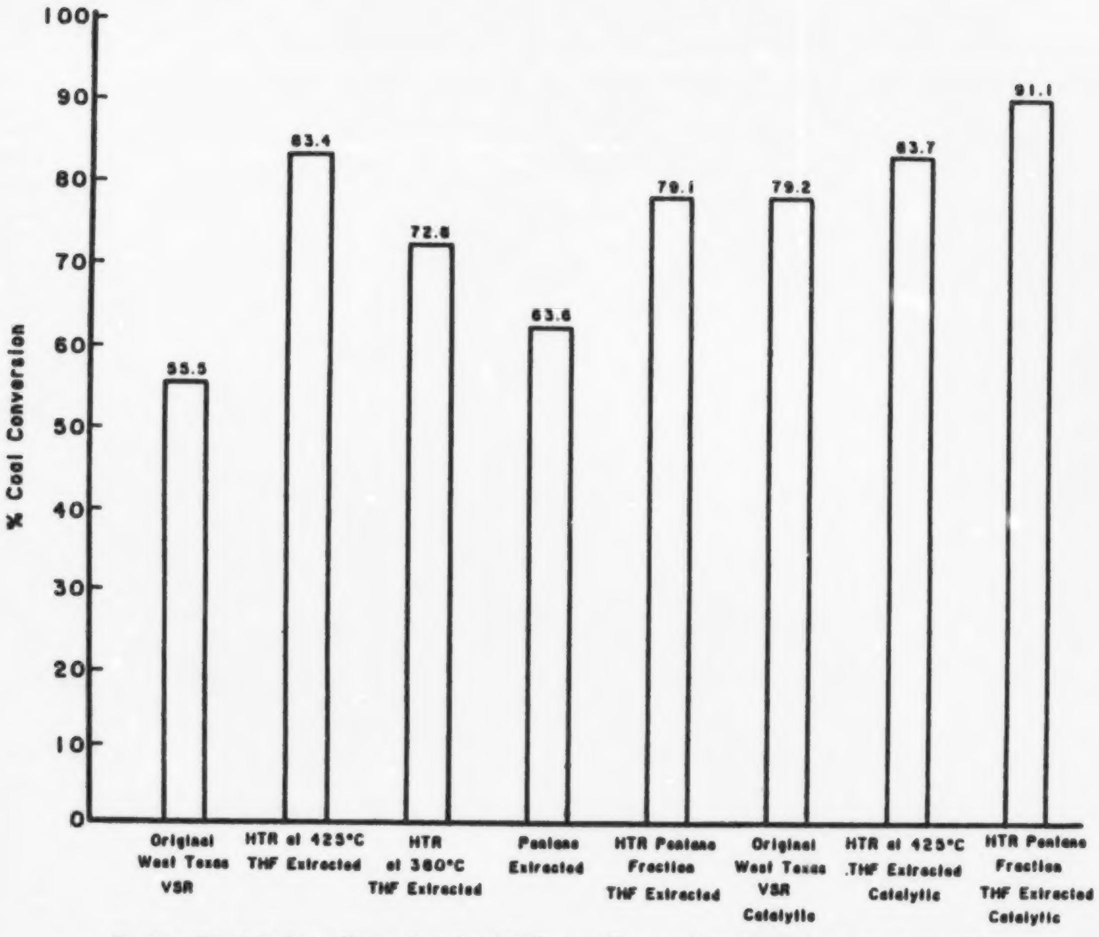


Fig.11 – Oil yield from thermal and catalytic reactions using pretreated West Texas VSR

SESSION V: PAPER 19

LIQUEFACTION COPROCESSING OF WYODAK SUBBITUMINOUS COAL

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ABSTRACT

Results from an exploratory experimental study of liquefaction coprocessing using Wyodak subbituminous coal and mid-Continental petroleum residuum from the United States are reported. The data suggest that relatively high C_4-850°F distillate yields and pyridine soluble coal conversion values can be achieved even at the mild liquefaction reaction conditions used in this work. An apparent synergism towards distillate production is noted when coal and petroleum residuum are processed simultaneously. This synergism is attributed to increased petroleum residuum reactivity in the presence of coal.

Results from two four-factor experimental designs show that gas atmosphere, distillate solvent composition and hydrogen donor ability, and use of a disposable catalyst all affect distillate yield and coal conversion. Finally, limited experimental work using a second U.S. petroleum residuum sample suggests that residuum properties strongly influence coprocessing performance.

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*denotes speaker

PRÉSENTATION 19

COTRAITEMENT DE LIQUÉFACTION DU CHARBON SUB-BITUMINEUX WYODAK

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Professeur adjoint de génie chimique
Université du Wyoming

RÉSUMÉ

Cette communication présente les résultats d'une étude expérimentale préliminaire sur la liquéfaction par cotraitement en utilisant un charbon sub-bitumineux Wyodak et un résidu de pétrole provenant du centre des États-Unis. Les données suggèrent qu'on peut réaliser des rendements de distillat C_4-850°F et des valeurs de conversion de charbon soluble à la pyridine, relativement élevés, même dans les conditions de réaction de liquéfaction douce, utilisées pour ce travail. On constate une synergie manifeste vers la production de distillat lorsqu'on procède au traitement simultané du charbon et du résidu de pétrole. Cette synergie est attribuée à une réactivité accrue du résidu de pétrole en présence du charbon.

L'utilisation d'un catalyseur d'oxyde de fer entraîne un accroissement du rendement de distillat C_4-850°F, de la conversion de charbon et de la consommation d'hydrogène. On constate toutefois que l'oxyde de fer influence peu les rendements de distillats tirés du résidu de pétrole, en l'absence du charbon. Un travail expérimental limité, en utilisant un deuxième échantillon de résidu de pétrole, suggère que les caractéristiques du résidu influencent nettement le rendement du procédé, déterminé par les rendements de produits et la conversion du charbon.

**indique le conférencier*

LIQUEFACTION COPROCESSING OF WYODAK SUBBITUMINOUS COAL

INTRODUCTION

Numerous direct coal liquefaction process configurations have been developed in recent years. Most have been designed to operate in solvent balance, so that only coal is fed to the overall process. Hydrogen requirements are met by gasifying a portion of the feed coal or heavy coal-derived residuum removed from the process as ash concentrate. Research by a number of investigators has shown that the use of high-boiling coal-derived residuum as a recycle solvent component significantly improves coal conversion, distillate yields, and plant operability (1-4). At the same time, depletion of petroleum reserves in the United States and elsewhere has forced refiners to process heavier crude oils containing large quantities of metals and high-boiling residuum. In many cases, conversion of these residua to distillate liquids using conventional petroleum catalytic cracking or hydrocracking technology is difficult.

While a typical petroleum residuum is hydrogen deficient relative to lighter petroleum cuts, it is hydrogen rich compared with coal-derived residua. This fact led researchers to believe that liquefaction in the absence of gaseous hydrogen would be possible if petroleum residua solvents were utilized in a once-through operation. Examples of such work can be found in the Japanese solvolysis research by Yamada and co-workers (5-9) and in results reported by Mobil (10-16). Additional solvolysis studies involving tar sands bitumen and heavy oils were conducted by Moschopedis and associates at the Alberta Research Council (17-18). Solvolysis can convert as much as 90 wt % of the feed coal to pyridine soluble material, but liquid products require extensive upgrading before use as distillate fuels.

The quality and quantity of distillate liquids derived from liquefaction coprocessing can be increased by providing gaseous hydrogen and a heterogeneous catalyst. Hydrocarbon Research, Inc. (19) patented a process utilizing H-coal ebullating catalyst bed technology to hydrocrack mixtures of coal and petroleum-derived residual oil at nominal H-coal liquefaction conditions of about 840°F and 2250 psig hydrogen pressure. Distillate yields as high as 60 to 65 wt % of the total coal-oil feed were obtained using Illinois No. 6 bituminous coal and Kuwait vacuum residuum in a petroleum residuum/coal weight ratio ranging between 1.0 and 2.0. Hydrogen consumption was approximately 3 wt % of the total residuum-coal feed. Conventional petroleum hydrogenation catalysts such as cobalt-nickel or cobalt-molybdate on alumina were used in the ebullating bed. It is unclear to what extent the petroleum residuum was converted in these experiments, since high distillate yields have been reported in conventional H-coal direct liquefaction processing (20,21). Nevertheless, this patent demonstrates the potential for obtaining large distillate yields from liquefaction coprocessing.

UOP, Inc. (22) developed and patented a process which converts both coal and heavy hydrocarbon liquids in the presence of a finely divided, unsupported metal hydrogenation catalyst. The patent recommends that metals or mixtures of metals on the catalyst be selected from groups IVB, VB, VIB, VIIB, and VIII in the Periodic Table of Elements. The primary objective of the UOP process is to convert coal to high-boiling liquid products while simultaneously reducing the asphaltene content of the petroleum residuum. No net distillate yield or hydrogen consumption data were reported in the UOP patent disclosure.

Chevron (23,24) has developed the Co-refining Process, a two-stage process scheme to simultaneously convert coal and heavy petroleum to lighter liquids. In the first stage, coal is dissolved in a petroleum solvent with an initial boiling point of about 500° to 600°F at temperatures in the range of about 750° to 900°F. No catalyst is used in this step. First-stage dissolver effluent consisting of dissolved coal, petroleum solvent, and insoluble solids is then hydrocracked with a conventional petroleum hydrocracking catalyst in a second stage operating at temperatures below 800°F. Hydrogen gas is present in both stages. Total C_4+ liquid product yields exceeding 110 wt % of total petroleum feed have been reported. These high yield values were attributed, in part, to inhibited coking of heavy petroleum fractions by the suspended coal particles. Significant demetallization of the residuum was also noted.

In more recent work, Curtis and co-workers at Auburn University in cooperation with Cities Service studied coprocessing of bituminous and subbituminous coals with six heavy crude oil samples using a tubing bomb microautoclave reactor system (25). They found that both hydrogen gas and heterogeneous hydrocracking catalyst such as nickel-molybdate on alumina were required to achieve reasonable coal conversion values. Tetralin was found to be a superior liquefaction solvent when compared to each of the six crude oil solvents at all coprocessing reaction conditions studied. This work once again suggests that petroleum-derived solvents are poor hydrogen donors.

The objective of the work described in this paper has been to explore various aspects of liquid fuel production from liquefaction coprocessing of Wyodak subbituminous coal and petroleum residuum. The effects of feed gas atmosphere, distillate solvent composition, and use of a disposable catalyst on process performance have been investigated using statistical experimental design techniques. Preliminary experiments demonstrating the effect of petroleum residuum quality and the existence of coal/residuum synergistic interactions were also included as part of the study.

EXPERIMENTAL

Wyodak subbituminous coal sample Wyo-3 was used as feed coal in the coprocessing experiments. Selected properties of the coal are presented in Table 1. This sample was obtained from the Anderson seam at the Carter Coal Company's Rawhide Mine located in the Powder River Basin of northeastern Wyoming. Sampling and preparation details of the coal have been reported (26,27).

Properties of two petroleum residua used in this work are shown in Table 2. Residuum A-1 is a nominal 750°F + boiling range fraction of high sulfur Wyoming crude oil obtained from the Sinclair Oil, Inc. refinery in Sinclair, Wyoming. Residuum A-2 is a nominal 850°F + boiling range fraction of a mid-Continental crude oil obtained from a proprietary source. As shown in Table 2, A-2 contains approximately 12 wt % asphaltenes, while A-1 is asphaltene-free.

Coal-derived solvent F-17B was used as distillate feed in some of the coprocessing runs. Properties of this solvent are shown in Table 3. The solvent is a nominal 500°-800°F boiling range, unhydrogenated fraction of Wyodak recycle solvent produced in 1975 at the Wilsonville, Alabama six-ton-per-day pilot plant. Previous work at the University of Wyoming has shown that F-17B is a less than adequate hydrogen donor solvent for Wyodak coal liquefaction (26).

Table 3 also lists the properties of solvent F-68, a simulated bottoms recycle solvent consisting of approximately 50 wt % low ash, Wyodak coal-derived SRC produced at Wilsonville in 1975, and 50 wt % F-17B. This mixture was mildly hydrogenated in a two-litre Autoclave Magnedrive II batch reactor at 700°F for one hour at an initial cold hydrogen pressure of 2000 psig. Nalcomo 477 cobalt-molybdate hydrotreating catalyst was used in the hydrogenation runs. Catalyst samples were thermactivated at 1000°F for approximately two hours in a muffle furnace prior to use. Mildly hydrotreated coal-derived bottoms recycle solvents, such as solvent F-68, have been found to be excellent liquefaction solvents for Wyodak coal in prior work at the University of Wyoming (26). As such, liquefaction results from runs using F-68 represent an appropriate base case to evaluate liquefaction coprocessing performance. No coprocessing experiments using mixtures of F-68 and petroleum asphalt were completed.

Additional coprocessing runs were made using tetralin as distillate solvent in place of F-17B. Piperidinopyridine, an extremely powerful nucleophile which has been shown to enhance coal dissolution in direct coal liquefaction, and m-cresol were used as distillate solvent components in some runs. All pure compounds used in this work were ACS reagent grade.

The liquefaction coprocessing experiments were carried out in a novel 60 cm^3 microautoclave reactor designed and built at the University of Wyoming. This reactor is similar to larger Autoclave batch reactors except that heating is accomplished with a high-temperature sandbath. At the end of each run, the reactor and its contents are quenched with an icewater bath. This reactor system can provide the quick heat-up (~2 min.) and cool-down (~30 sec.) characteristics of small tubing bomb reactors, while at the same time ensuring sufficient mechanical agitation of the reactants with an Autoclave Magnedrive II stirring assembly to minimize hydrogen mass transfer effects. Furthermore, the system is designed so that the reactor pressure is very nearly constant throughout an experiment.

Reaction conditions in this study were fixed at 800°F reaction temperature, 2000 psig initial cold hydrogen pressure or 1000 psig initial cold carbon monoxide pressure, and 15 minutes reaction time. Distilled water in an amount equal to 50 wt % of the dry feed coal was added to runs using a carbon monoxide atmosphere. Iron oxide (Fe_2O_3) provided by the Kerr-McGee Corporation was used in some runs at a concentration of 5 wt % of the dry feed coal. An analysis of this iron oxide catalyst is shown in Table 4. Effects attributable to the use of hydrogen sulfide as a homogeneous catalyst were studied by adding carbon disulfide to the reactor feed of selected runs in an amount equal to approximately 5 wt % of the dry feed coal. The coal:residuum:distillate weight ratio was held at 1:1:1 in all runs. These feed ratios and mild reaction conditions were selected so that measurable differences in the effects of reactants and catalysts on net C_4-850°F distillate yield and pyridine soluble coal conversion could be detected. Gaseous products were analyzed using gas chromatography. Water and distillate yields were measured by distilling portions of the combined liquid-solid product mixture to an 850°F end point in a microdistillation apparatus. Additional portions of the liquid-solid product mixture were extracted in a Soxhlet extraction apparatus using cyclohexane, toluene, and pyridine. These analyses allowed the products listed in Table 5 to be monitored for each run.

RESULTS

Before proceeding with a discussion of the experimental design results, some preliminary data comparing the performance of liquefaction coprocessing with direct coal liquefaction are presented. All yield and conversion data are reported as a percentage of moisture- and ash-free coal charged. Figure 1 summarizes results of liquefying Wyo-3 coal in distillate solvent F-17B with or without the addition of residuum A-2. Increased distillate yield but decreased hydrogen consumption and pyridine soluble coal conversion were achieved when the coal and residuum were coprocessed.

A similar trend is noted in Figure 2 where the coprocessing data is compared with yield and conversion data from simulated bottoms recycle liquefaction using F-68 bottoms recycle coal-derived solvent. At the reaction conditions studied, coprocessing distillate yields were significantly higher than the corresponding yields from bottoms recycle runs. The fact that both hydrogen consumption and coal conversion were lower during coprocessing suggests that a significant portion of the distillate was derived from petroleum residuum. To further explore this hypothesis, a series of runs was completed in which no coal was added to the reactor. All other reaction conditions were the same as in the coprocessing runs. As shown in Figure 3, A-2 residuum did not convert to distillate in the absence of coal at the mild reaction conditions studied. No significant increase in residuum conversion was noted when iron oxide catalyst was added. Thus, it seems that the apparent residuum reactivity towards distillate production is caused by the coal or possibly primary coal-derived products present in the reaction mixture. Other researchers have alluded to such a coal-residuum interaction (24). One hypothesis would suggest that reactive coal fragments produced during coal depolymerization may attack and weaken bonds within the complex residuum structure, thereby increasing residuum reactivity. A possibility also exists that the coal or coal mineral matter in some way acts as a catalyst in petroleum residuum conversion. At least one reference in the German patent literature describes a process in which petroleum vacuum bottoms are hydrocracked to distillate using 1 wt % subbituminous coal as catalyst (28). The coal had been impregnated with $FeSO_4$ prior to use, so it is not obvious exactly what effect the coal itself had on conversion of the vacuum bottoms.

Because of the exploratory nature of this work, statistical experimental design techniques were used to explore the effects of feed gas atmosphere, distillate solvent composition, and use of a disposable catalyst on liquefaction coprocessing performance. As described in Table 6, individual four-factor two-level experimental design were organized for factors (or variables) A, B, C, and D and E, F, G, and H, respectively. All sixteen experiments were completed in each design. Error estimates were obtained by performing replications of several selected run combinations.

Results of the factorial design experiments are summarized in Table 7. Both C_4-850°F distillate yield and pyridine soluble coal conversion were used as the dependent variables upon which effects of the independent design variables were determined. As indicated in the table, the main effect of each variable in each design was found to be statistically significant at a 95% confidence level. Each positive or negative sign indicates the average relative change in yield or conversion when that design variable was changed from the low to high level. Thus, it can be seen that changing the gas atmosphere from hydrogen to carbon monoxide plus water generally reduced both distillate yield and conversion. Other researchers (29) have reported increased liquefaction reactivity using CO/H_2O, so it is likely that the reaction conditions arbitrarily chosen for the present study were not optimal for the water gas shift reaction to proceed.

Use of a good hydrogen donor solvent (tetralin) rather than F-17B improved both distillate yield and coal conversion. This result suggests the possible need for recycling a hydrogen-rich process-derived stream to be mixed with fresh coal and petroleum residuum if maximizing distillate yield is a process objective. Addition of either iron oxide or hydrogen sulfide also resulted in increased distillate yield and coal conversion. Since similar results have been reported when these two catalysts were used in direct coal liquefaction of Wyodak coal (30), it is not clear whether the yield improvement can be attributed solely to increased coal conversion or whether increased residuum conversion also occurs.

Finally, results of the experiments using piperidinopyridine and m-cresol as distillate solvent components demonstrate the important role of nitrogen and oxygen functionalities in liquefaction coprocessing. Further model compound studies are underway to investigate the role of coal, primary coal-derived products, and possibly distillate solvent on residuum conversion to lighter boiling products.

If, as suggested in Figures 1-3, the petroleum residuum acts as a reactant and not simply as a hydrogen donor or physical solvent for the coal, then residuum quality should also affect process yields and possibly coal conversion. To investigate this hypothesis, several experiments were completed using Wyo-3 coal and either A-1 or A-2 petroleum residuum. Figures 4 and 5 compare the yield and conversion results for these runs. It is apparent that A-2 residuum converts more readily than A-1 with or without iron oxide catalyst added. Coal conversion appears to be unaffected by residuum quality in the absence of iron oxide. These results indicate the importance of petroleum residuum reactivity on overall liquefaction coprocessing performance. Many more residuum samples would have to be studied to quantify this effect.

SUMMARY AND CONCLUSIONS

Various aspects of coprocessing Wyodak subbituminous coal and petroleum residuum have been examined at a fixed set of reaction conditions. Based on results of this work, the following tentative conclusions can be drawn:

1. Coprocessing of coal and petroleum residuum gave higher distillate yields but lower hydrogen consumption and coal conversion compared with direct liquefaction of coal at the same reaction conditions.
2. Petroleum residuum A-2 converted to distillate in the presence of Wyodak coal but not in the absence of the coal. This suggests the possibility of a synergism between the residuum and coal or primary coal-derived products.
3. Experimental design studies were used to demonstrate the importance of feed gas atmosphere, distillate solvent composition and hydrogen donor ability, and use of a disposable catalyst in maximizing distillate yield and coal conversion from liquefaction coprocessing.
4. Properties of the feed petroleum residuum affect distillate yield, hydrogen consumption, and to some extent coal conversion in the process.

ACKNOWLEDGEMENT

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TABLES

Table 1 – Properties of Wyodak subbituminous coal

Sample	Wyo-3
Mine	Rawhide
Seam	Anderson
Ultimate analysis (wt % dry basis)	
Carbon	58.2
Hydrogen	4.3
Nitrogen	0.8
Sulphur	2.9
Oxygen (difference)	13.9
Ash	19.9
Proximate analysis (wt % dry basis)	
Ash	19.9
Volatile matter	45.1
Fixed carbon	35.0

Table 2 – Properties of petroleum residua

Feed	A-1	A-2
Source	Sinclair	Mid-continental
Wt % distilled		
Water	0.0	0.0
350°F-	0.0	0.0
350-500°F	0.0	0.0
500-650°F	0.0	0.0
650-850°F	13.1	3.4
850°F +	86.9	96.6
Ultimate analysis (wt %)		
Carbon	84.9	85.7
Hydrogen	10.6	8.8
Nitrogen	0.5	1.3
Sulphur	3.8	2.2
Oxygen (difference)	0.2	2.0
Cyclohexane solubility, wt %	100.0	88.2
Toluene solubility, wt %	100.0	100.0
Pyridine solubility, wt %	100.0	100.0

Table 3 – Properties of Wyodak coal-derived solvents

Feed	F-17B	F-68
Source	Wyodak coal	Wyodak coal
Wt % distilled		
Water	0.0	0.0
350°F-	0.0	1.0
350-500°F	2.1	1.5
500-650°F	63.7	27.5
650-850F	31.2	19.8
850F +	3.0	50.2
Ultimate analysis (wt %)		
Carbon	87.5	86.8
Hydrogen	7.7	7.1
Nitrogen	0.7	0.7
Sulphur	0.3	0.2
Oxygen (difference)	3.8	5.2
Cyclohexane solubility, wt %	94.1	65.4
Toluene solubility, wt %	96.9	84.0
Pyridine solubility, wt %	100.0	99.4

Table 4 – Analysis of Kerr-McGee iron oxide catalyst

	Wt %
Fe_2O_3	83.8
FeO	3.7
TiO_2	0.5
Cl –	4.23
Unidentified	7.77
	100.00

Table 5 – Products monitored in coprocessing experiments

Gases	
	CO, CO_2, H_2 C_1-C_3
Water	
C_4-850°F Distillate	
850°F + Pyridine soluble residuum	
	Oils Asphaltenes Preasphaltenes
Pyridine insoluble organic matter (IOM)	

Table 6 – Factorial design of experiments

Design #1

Factor	Levels: O	Levels: 1
(A) Gas atmosphere	H_2	CO/H_2O
(B) Distillate solvent	F-17B	Tetralin
(C) Disposable catalyst	None	Fe_2O_3
(D) Additive to distillate solvent	None	Piperidinopyridine

Design #2

Factor	Levels: O	Levels: 1
(E) Gas atmosphere	H_2	CO/H_2O
(F) Distillate solvent	F-17B	Tetralin
(G) Disposable catalyst	None	H_2S (as CS_2)
(H) Additive to distillate solvent	None	m-cresol

Table 7 – Statistically significant main effects from experimental design studies (95% confidence level)

Design #1

Factor	Yield Effect	Conversion Effect
A	–	–
B	+	+
C	+	+
D	+	+

Design #2

Factor	Yield Effect	Conversion Effect
E	–	–
F	+	+
G	+	+
H	+	–

FIGURES

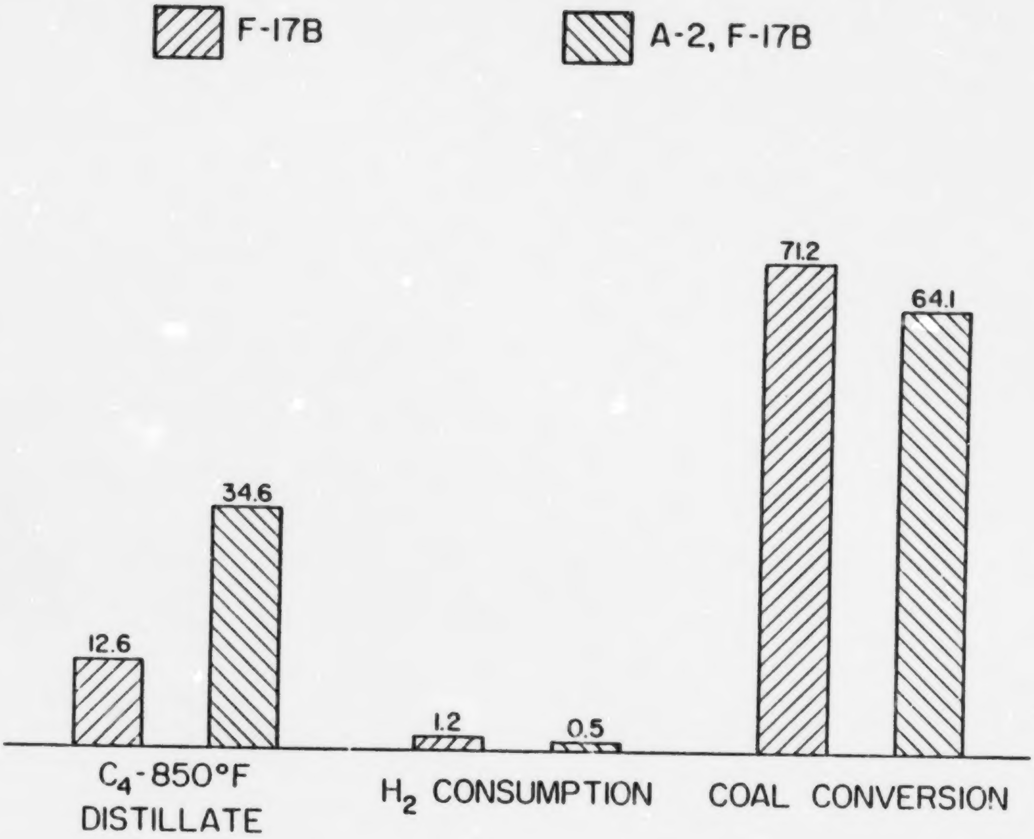

Fig. 1 – Comparison between direct liquefaction and coprocessing of Wyodak coal

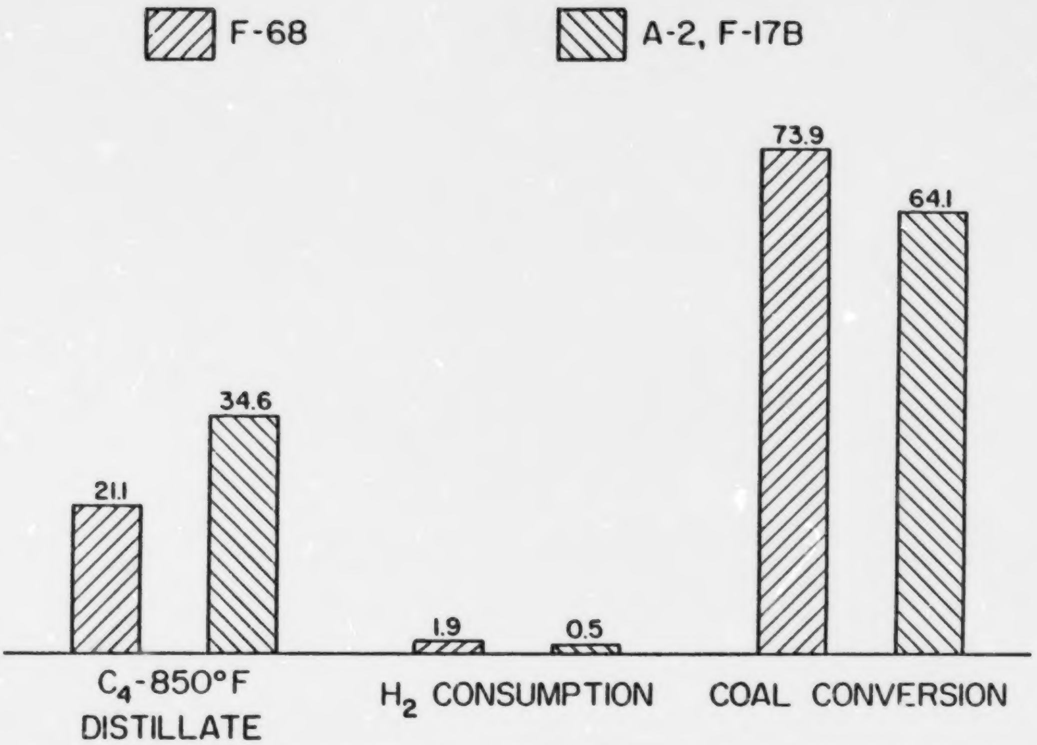

Fig. 2 – Comparison between simulated bottoms recycle liquefaction and coprocessing of Wyodak coal

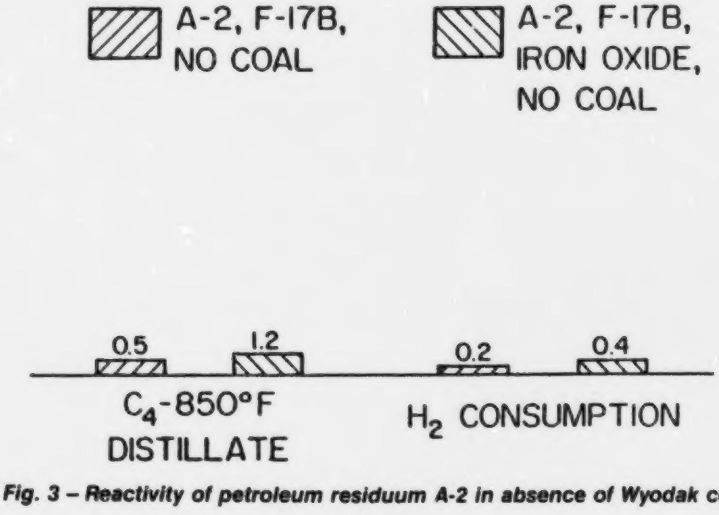

Fig. 3 – Reactivity of petroleum residuum A-2 in absence of Wyodak coal

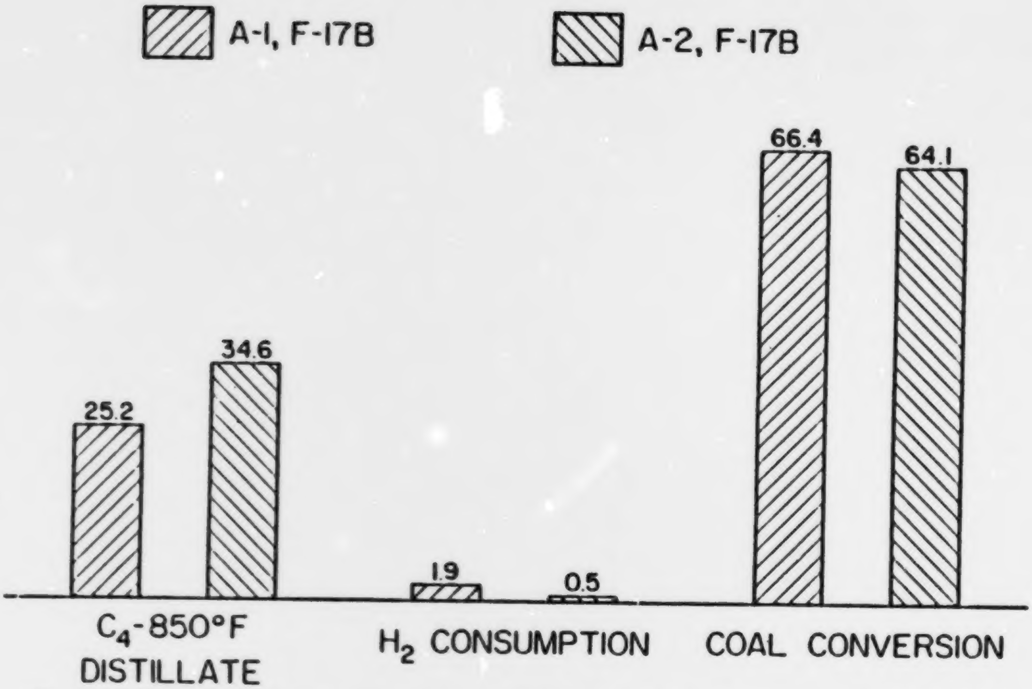

Fig. 4 – Comparison between coprocessing of Wyodak coal with petroleum residua A-1 and A-2

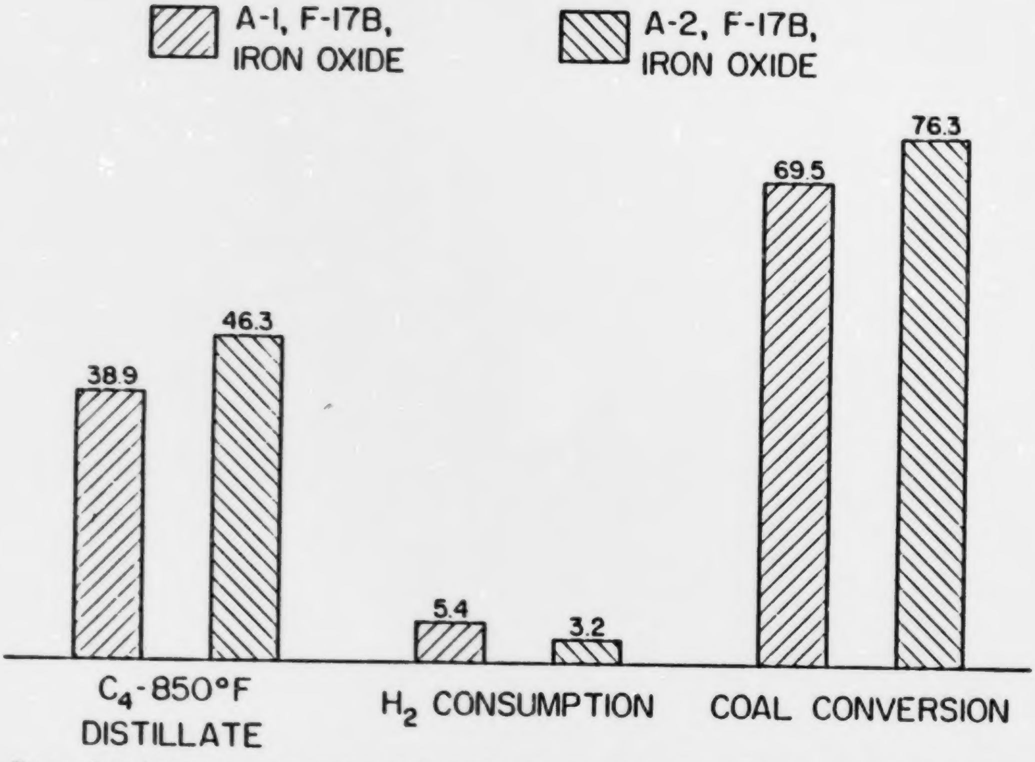

Fig. 5 – Comparison between coprocessing of Wyodak coal with petroleum residua A-1 and A-2 in the presence of iron oxide catalyst

SESSION V: PAPER 20

TWO-STAGE LIQUEFACTION OF SUBBITUMINOUS ALBERTA COALS IN NON-DONOR SOLVENT

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ABSTRACT

Though high oxygen content increases the liquefaction reactivity of low rank coals, it also results in high hydrogen consumption, particularly in the presence of effective hydrogen donor solvents or very active catalysts. Under conditions of efficient transfer of hydrogen facilitated by the donor and/or catalyst, most of the organic oxygen present in the coal evolves in the form of water.

Results of experimental work carried out at the Alberta Research Council have shown that pretreatment of subbituminous Alberta coals in bitumen with an appropriately formulated mix of carbon monoxide and water, in the presence of alkali metal carbonates, and at a relatively low temperature of 380-400°C, resulted in rapid solubilization of coal in bitumen, removal of about 80% of organic oxygen in the form of carbon dioxide, and substantial addition of hydrogen to the product. Experimental evidence has been accumulated showing that coal-bitumen interaction results in a synergistic effect which increases distillable oil yield, suppresses generation of coke and reduces hydrocarbon gas production. The product of reacting the coal and bitumen with carbon monoxide/steam mixture appeared to be susceptible to further hydrogenation with gaseous hydrogen. During preliminary tests, up to 90% (on daf bitumen) of hydrogen-rich distillable oil was produced. This novel approach to processing high oxygen content subbituminous coals in a poor hydrogen donor solvent in a once-through process mode is being evaluated in batch autoclaves and semi-continuous experimental units. Some of the results of these tests are presented and the main pathways of process chemistry are discussed.

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PRÉSENTATION 20

LA LIQUÉFACTION EN DEUX ÉTAPES DES CHARBONS SUB-BITUMINEUX DE L'ALBERTA DANS UN SOLVANT NON-DONNEUR

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RÉSUMÉ

Même si la forte teneur en oxygène accroît la réactivité à la liquéfaction des charbons de faible rang, elle se traduit également par une forte consommation d'hydrogène, notamment en présence de solvants donneurs réels d'hydrogène ou de catalyseurs très actifs. Dans des conditions de transfert efficace d'hydrogène facilitées par le donneur et/ou le catalyseur, la plus grande partie de l'oxygène organique présent dans le charbon se transforme en eau.

Les résultats des travaux expérimentaux effectués au Conseil de recherche de l'Alberta ont démontré que le prétraitement des charbons sub-bitumineux de l'Alberta, en bitume, avec un mélange approprié d'oxyde de carbone et d'eau, en présence de carbonates métalliques alcalins et à une faible température de 380 à 400°C, se traduit par la dissolution rapide du charbon en bitume, la récupération d'environ 80 p. 100 de l'oxygène organique sous forme d'anhydride carbonique, et l'addition substantielle d'hydrogène au produit. Les données expérimentales accumulées indiquent que l'interaction charbon-bitume se traduit par un effet de synergie qui accroît le rendement de pétrole distillable, neutralise la génération de coke et réduit la production de gaz d'hydrocarbures. Le produit découlant de la réaction du charbon et du bitume avec le mélange oxyde de carbone/vapeur semblait se prêter à une hydrogénation plus poussée avec l'hydrogène gazeux. Lors d'essais préliminaires, on a produit jusqu'à 90 p. 100 (sur du bitume daf) de pétrole distillable riche en hydrogène. Cette nouvelle façon de procéder au traitement des charbons sub-bitumineux ayant une forte teneur en oxygène, dans un solvant donnant peu d'hydrogène, en utilisant un procédé à passe unique, a fait l'objet d'une évaluation détaillée grâce à des essais en autoclaves et dans des installations expérimentales en semi-continu. Les résultats de ces essais sont présentés et les principales voies offertes par le traitement chimique sont discutées.

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TWO-STAGE LIQUEFACTION OF SUBBITUMINOUS ALBERTA COALS IN NON-DONOR SOLVENT

INTRODUCTION

Basic studies carried out at Alberta Research Council during 1975-79 on mild solvolysis of Cretaceous and Carboniferous coals of different degrees of coalification using vehicle solvents, characterized by various hydrogen-donating capacity (1) have furnished evidence that, though high oxygen Alberta subbituminous coals could be effectively solubilized with donor solvents, the solvolysis was accompanied by extensive generation of water. In fact, the amount of generated water tended to increase with the increasing hydrogen-donating capacity of the vehicle donor solvent. It appears that application of a highly efficient catalytic system for hydrogenation of subbituminous coal also leads to extensive generation of water (2).

The high reactivity of carbon monoxide with low rank coals has been known for some time (3). Experiments at the Research Council showed that Alberta subbituminous coals could be effectively solubilized with carbon monoxide/steam mixtures and that this solubilization technique did not require solvents characterized by good hydrogen-donating capacity.

Application of bitumen as a solvent for liquefaction of Alberta subbituminous coals in hydrogen atmosphere was initiated by Boomer and Saddington of the Alberta Research Council and University of Alberta (4) and subsequently pursued by others (5, 6). Results of recent tests carried out at the Research Council (6) indicate that hydrogen treatment at 425-480°C resulted in considerable coking of coal bitumen mixtures and at lower reaction temperatures (390-415°C), very long residence time was required to complete the solubilization process.

The studies conducted at the Research Council during 1980-82 on solubilization of indigenous subbituminous coals in anthracene oil and bitumen (7, 8) in the presence of carbon monoxide steam mixtures have shown that, in terms of kinetics and coal solubilization yields, the optimum reaction temperatures appear to be below 400°C and the products of solvolysis in bitumen are very susceptible to further hydrogenation with hydrogen.

The above findings led to formulation of the concept of liquefying Alberta subbituminous coals in a two-stage process (first stage – solubilization with CO/steam in bitumen; second stage – catalytic hydrogenation). An experimental program aimed at detailed evaluation of this concept was started in 1982 and some of the results obtained during program development are reported in this presentation.

EXPERIMENTAL

The experiments were carried out in a standard batch autoclave system and in a hot charge/discharge unit – a system specifically designed and commissioned for studying the mechanism and kinetics of two-stage liquefaction processes.

Batch Autoclave System

The batch autoclave experiments were carried out in 1-litre magnestirred autoclaves (manufactured by Autoclave Engineers Ltd.) with internal cooling coils.

The coal/bitumen slurry was charged into an autoclave at room temperature followed by pressurizing the system with carbon monoxide (7 MPa) or hydrogen (10.5 MPa). The autoclave was heated to a selected temperature, maintained at this temperature for a required period of time, then cooled down and discharged. Gas samples were analyzed using a CARLE IIIH gas chromatograph. Liquid and solid products were separated by distillation and extraction methods. The liquids were separated into three fractions: naphtha (IBP-240°C), gas oil (240-525°C) and pyridine extract (+525°C). Coal conversion was calculated on the basis of pyridine insoluble organic material. The distillables and pyridine solubles were subjected to ultimate, spectral and class analyses.

Hot Charge/Discharge Unit (HCDU)

The HCDU (see Fig. 1) consists of 2- and 1-litre magnestirred reactors and a high-pressure vessel to collect the product slurry. The first reactor operates in a batch mode and the second in a semi-continuous mode.

A properly formulated charge of coal/bitumen, water, and catalyst (K_2CO_3 and K_2MoO_4) was placed into the first reactor (R1) at room temperature. The reactor was pressurized with carbon monoxide (8.75 MPa) and heated to 390°C. The contents were reacted at this temperature for 30 minutes and the gaseous products were discharged at reaction temperature, passed through a condenser (immersed in ice-water) and analyzed in the CARLE IIIH gas chromatograph. The R1 reactor was purged with hydrogen and then the slurry was pneumatically transferred to the second reactor (R2) which had been preheated to the reaction temperature (420-480°C). In the R2 reactor, the slurry was contacted for 30 to 90 minutes with a continuous flow of hydrogen (2 s1pm) at 17.5 MPa. The outlet gases, after passing through the condenser immersed in ice-water, were continuously analyzed using the gas chromatograph. The product slurry from the second reactor was pneumatically transferred to the discharge vessel where it was depressurized and quenched in a nitrogen atmosphere.

The product work-up procedure and product analyses were the same as described above for batch autoclave tests.

RESULTS AND DISCUSSION

Results of the analyses of Alberta subbituminous coals and Suncor bitumen, tested in these studies, are presented in Tables 1 and 2. The ash oxygen contents of the coals vary from 10.7–30.3% and from 16.9–24.4%, respectively. Except for the Tofield coal, the sulphur content appears to be quite low for all tested coals; however, for Suncor bitumen it reaches 4.5%.

The block diagram of the Alberta Research Council two-stage CO/steam-H_2 coal/bitumen process (9, 10) is presented in Figure 2. The major difference between the conventional coprocessing scheme and the one proposed is based on including into the ARC scheme the process of agglomeration of subbituminous coal with bitumen-derived liquids and application of CO/steam gas for pretreatment of coal-bitumen mixture prior to reacting it with hydrogen.

Agglomeration of coal with bitumen-derived bridging liquid under conditions described elsewhere (11) results in dramatic reduction of mineral matter content in the flocculated product. Fine grinding of coal, required for effective mineral matter removal, is carried out in water/oil paste, and the agglomerated flocs, containing 25-30% water, are subjected directly to CO/steam treatment. This prevents the oxidation of the feed-coal [oxidation has a very deleterious effect on coal hydrogenation (12)] and eliminates the need for coal drying because the amount of water deposited on the flocs is slightly below the concentration required for optimum performance of the CO/steam reactor.

The important factors in favour of CO/steam (instead of hydrogen) treatment of the subbituminous coal/bitumen blends in the first stage of a two-stage process are: high deoxygenation, rapid kinetics of solvolysis, very high solubilization yields regardless of the origin and hydrogen reactivity of the subbituminous coal tested, and the occurrence of a remarkable synergistic effect.

Table 3 presents the elemental balances obtained as a result of coprocessing of Alberta subbituminous coal and Suncor bitumen with CO/steam and, independently, with hydrogen under identical temperature and residence time conditions. The tests with bitumen and hydrogen were conducted with iron-based catalyst. The data demonstrate that CO/steam pretreatment is more effective in terms of oxygen removal and leads to significantly lower carbon loss compared with hydrogen pretreatment. Most interesting is the finding that CO/steam treatment hydrogenates the coal/bitumen feed more effectively than hydrogen does (Table 3 – H/C ratios). The residence time required for completion of the CO/steam treatment could be reduced by a factor of 2.5 (compared to hydrogen treatment) without any adverse effects in terms of coal solubilization yields and liquid products' quality and yields.

The benefits (deoxygenation and hydrogenation) of the CO/steam reaction used for the coal/bitumen blend do not occur when bitumen is treated alone (without coal addition). Treatment of bitumen alone with CO/steam yields results comparable to those obtained in a nitrogen/steam atmosphere (Table 4). Treatment of coal/bitumen slurry in nitrogen/steam atmosphere results in very low coal conversion values (a few percent only), thus confirming the poor hydrogen donating capacity of the bitumen.

Studies conducted at Alberta Research Council on pretreatment of subbituminous coal/bitumen blends with CO/steam and, independently, with hydrogen resulted in accumulation of considerable evidence that the synergistic effect occurring on reacting coal with bitumen is particularly enhanced in the presence of CO/steam atmosphere (see Table 5). It has been found that in this atmosphere, the generation of volatile hydrocarbons (C_1-C_4) was drastically suppressed on addition of coal bitumen. In fact, for all coals tested (see Table 5, column 3), the addition of coal to bitumen resulted in the generation of much lower quantities (negative numbers) of C_1-C_4 hydrocarbons compared to C_1-C_4 quantities generated by an identical amount of bitumen treated in the absence of coal. When hydrogen, instead of CO/steam, was used for pretreatment, the effect of suppression of gaseous hydrocarbons' generation was of marginal significance only (Table 5, column 7).

Even more explicit evidence of the occurrence of the synergistic effect on processing coal/bitumen blends in CO/stream, as opposed to hydrogen atmosphere, emerges from comparing the values obtained by subtracting the (corrected for blank tests) liquid yield values from total coal conversion values (Table 5, columns 5 and 9). Provided no major interaction takes place between coal and solvent, the liquid yields should always be lower (by 10-20% weight) compared to the respective coal conversion values; this is a consequence of elimination of some heteroatoms and the loss of volatile hydrocarbons occurring on reductive treatment of coal. However, the values presented in column 9 (Table 5) are, on average, significantly above the 20% mark, thus indicating that the chemistry between the coal and bitumen, in the presence of hydrogen, has an adverse effect on conversion of coal to liquid products. The values obtained for CO/steam treatment, presented in column 5 (Table 5), vary between -3 and 16 and give evidence that there was a beneficial interaction between the coal and bitumen, while the interaction between coal and bitumen in hydrogen atmosphere was generally detrimental in terms of total liquid yields.

Products from CO/steam treatment of coal/bitumen mixture appeared to be very susceptible to further hydrogenation. Figure 3 presents the initial results of two-stage processing of the bitumen and coal/bitumen blend in the hot charge/discharge unit in the presence of a disposable catalyst.

The yield of distillable oils approaches 90% (on daf bitumen) and the major portion of the product-oil boils below 375°C. The elemental compositions of the main liquid and solid products and, for comparison, the feed material, are presented in Table 6. The distillable products are rich in hydrogen and low in nitrogen and oxygen contents. It is noteworthy that removal of oxygen takes place in the first stage of the reaction and only very small quantities of oxygen are removed on treatment with hydrogen (second stage).

Under present reaction conditions, two-stage processing yields about 15-20% of the total organic feed (on daf basis) in the form of pyridine soluble material, which can be partially converted into distillable products on further processing. Development of a catalytic system that would enhance this conversion directly in the hot charge/discharge unit under mild reaction conditions (less gas evolution) is the main objective of the catalytic hydrogenation optimization studies carried out at the Council.

CONCLUSIONS

A process specifically designed for upgrading the extensive reserves of Alberta subbituminous coals, bitumen and heavy oil is being evaluated at the Alberta Research Council. The once-through process concept eliminates the need for recycling the oil, is characterized by high hydrogen economy, and takes advantage of the synergistic effect occurring in coal/bitumen coprocessing. The process generates high-quality oils for which, as it is expected, only limited upgrading will be required. Main emphasis in development of the process is being placed on the selection of an efficient catalytic system for the (second) hydrogenation stage.

The application of carbon monoxide in this process appears to have a major beneficial effect on its performance. This beneficial effect will have to be weighed against the cost of the capital equipment required for carbon monoxide (as opposed to hydrogen) generation and purification, and will be a subject of separate economic feasibility studies.

ACKNOWLEDGEMENT

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Contributions made by Dr. T. Lee, Ms. L. Black and Mr. D. Aitchison are very much appreciated.

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TABLES

Table 1 – Proximate and ultimate analyses of Alberta subbituminous coals

Coal	Volatile matter % maf	Fixed Carbon % maf	Ash % dry	Ultimate analysis (% maf)					
				C	H	N	S	O diff	H/C
Smoky Tower	43.4	56.6	20.7	75.8	5.1	1.7	0.5	16.9	0.81
Highvale	39.6	60.4	11.4	75.0	4.3	1.1	0.2	19.4	0.69
Vesta Mine	41.9	58.1	12.4	74.4	5.0	1.5	0.6	18.5	0.81
Ardley	39.3	60.7	20.0	75.7	4.2	1.1	0.5	18.5	0.67
Judy Creek Washed	40.5	59.5	15.3	75.1	4.1	0.9	0.4	19.5	0.65
Fox Creek Washed	40.0	60.0	16.5	75.8	4.2	1.1	0.5	18.4	0.66
Pickardville	43.2	56.8	14.6	72.8	4.5	1.3	0.4	21.0	0.74
Tofield	46.3	53.7	25.4	73.8	4.6	1.7	1.2	18.7	0.75
Battle River S.	48.8	51.2	30.3	68.4	5.1	1.4	0.7	24.4	0.89

Table 2 – Ultimate analysis of solvent (bitumen)

Material	Composition % wt as received					
	C	H	N	O*	S	H/C
Suncor bitumen Athabasca deposit	81.3	10.3	0.4	1.1	4.5	1.52

* *Direct determination*

Table 3 – Elemental balances* – coprocessing of Alberta subbituminous coal and Suncor bitumen with CO/steam and H_2 at 400°C, 1 hr residence time

Process type	Feed (g)						Liquid yields (g)						Elements removal $\frac{\text{in-out}}{\text{in}} \times 100$		
		O	S	C	H	H/C		O	S	C	H	H/C	O	S	C
CO/steam	Coal	9.96	0.21	34.51	2.15	0.75	Naphtha	0.01	0.10	3.73	0.61	1.96	78	19	5
	Bitumen	1.40	5.60	101.75	12.87	1.52	Gas Oil	0.14	1.51	48.74	6.72	1.65			
							Extract	2.34	3.09	76.74	8.16	1.28			
	Total	11.36	5.81	136.26	15.02	1.32	Total	2.49	4.70	129.21	15.49	1.44			
Hydrogenation	Coal	10.56	0.22	36.58	2.28	0.75	Naphtha	0.23	0.20	12.17	1.95	1.92	58	39	8
	Bitumen	1.40	5.60	101.83	12.88	1.52	Gas Oil	0.75	0.98	37.11	4.75	1.53			
							Extract	4.01	2.38	78.08	7.93	1.22			
	Total	11.96	5.82	138.41	15.16	1.31	Total	4.99	3.56	127.36	14.63	1.38			

* *The average value from three runs in each process type*

Table 4 – Processing of Suncor bitumen with CO/steam and N_2/steam under the same reaction conditions

Products	% wt on daf solvent				
Process type	Naphtha	Gas oil	Extract	Total liquids	Volatile hydrocarbons
CO/steam*	9.9	41.9	36.6	88.5	5.1
N_2/steam	9.7	33.5	39.7	82.9	8.1

* *Mean value of three runs*

Table 5 – Conversions, liquid yields and gaseous hydrocarbons yields (% weight on daf coal) for Alberta subbituminous coals liquefied either with CO/steam or hydrogen at 400°C* with Suncor bitumen as a solvent

Coals	CO/steam liquefaction				Hydrogen liquefaction			
	Liquid yield	Vol. hydr.	Coal conv.	Coal conv. – liquid yield	Liquid yield	Volat. hydr.	Coal conv.	Coal conv. – liquid yield
Tofield	98	−3.1	95	−3	95	−1.7	96	1
Vesta	95	−4.9	96.5	1.5	71	2.7	95	24
Picardville	95	−7.0	95	0	84	−4.2	94	10
Smoky Tower	82	−3.9	85	3	57	2.4	84	27
Battle River S.	78	−4.9	94	16	79	−1.5	92.5	13.5
Ardley	79	−4.8	81	2	50	3.0	74.5	24.5
Fox Creek (w)**	77	−1.5	87	10	52	3.9	84	32
Highvale	76	−2.9	84	8	44	2.5	83	39
Judy Creek (w)**	72	−2.5	85.5	13.5	56	2.3	82.5	26.5

* *Liquid yields and gaseous hydrocarbons yields were corrected for blank tests*

** *Washed coal*

Table 6 – Elemental compositions* of the feed material (coal/bitumen blend) and the main liquid and solid products obtained from coprocessing in the hot charge/discharge unit

	C	H	N	O	S
Coal/bitumen blend	80.0	8.7	0.8	7.2	3.3
Naphtha (−200°C)	83.0	13.1	0.3	1.8	1.8
Middle oil (200-375°C)	85.4	11.1	0.2	1.2	2.1
Heavy oil (375-525°C)	85.6	10.5	0.4	1.3	2.2
Residue (+525°C)	86.1	8.0	1.1	2.9	1.9

* *on daf matter*

FIGURES

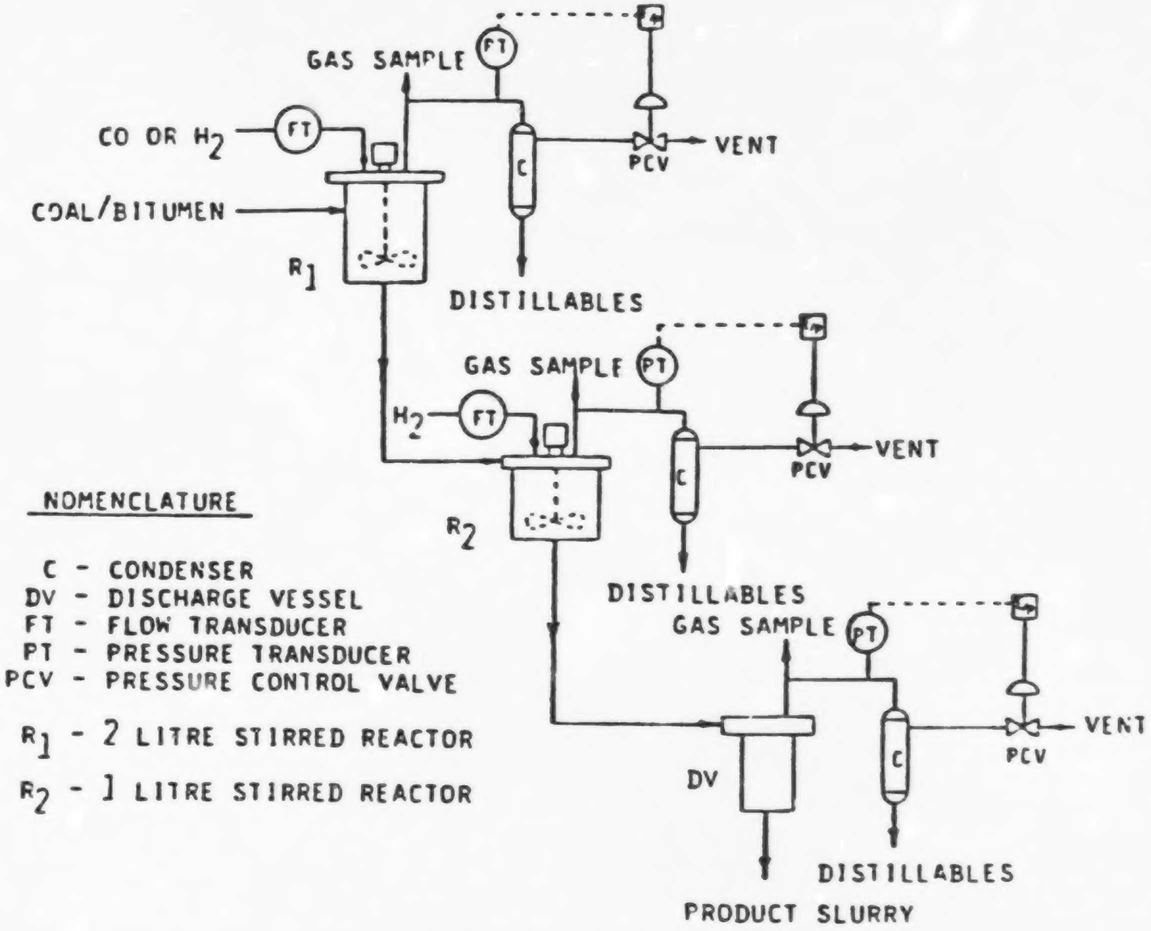
GAS SAMPLE
FT
CO OR H_2
FT
VENT
PCV
C
COAL/BITUMEN
R_1
DISTILLABLES
GAS SAMPLE
PT
H_2
FT
VENT
PCV
C
NOMENCLATURE
C - CONDENSER
DV - DISCHARGE VESSEL
FT - FLOW TRANSDUCER
PT - PRESSURE TRANSDUCER
PCV - PRESSURE CONTROL VALVE
R_1 - 2 LITRE STIRRED REACTOR
R_2 - 1 LITRE STIRRED REACTOR
R_2
DISTILLABLES
GAS SAMPLE
PT
VENT
PCV
C
DV
DISTILLABLES
PRODUCT SLURRY

Fig. 1 – Semicontinuous hot charge/discharge unit

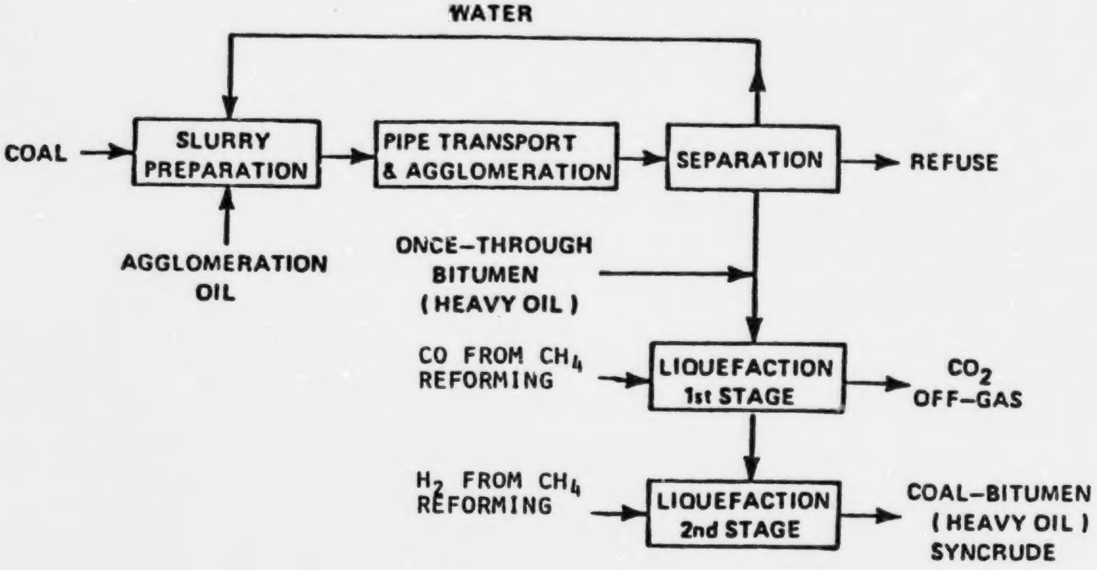
WATER
COAL
SLURRY PREPARATION
PIPE TRANSPORT & AGGLOMERATION
SEPARATION
REFUSE
AGGLOMERATION OIL
ONCE-THROUGH BITUMEN (HEAVY OIL)
CO FROM CH4 REFORMING
LIQUEFACTION 1st STAGE
CO2 OFF-GAS
H2 FROM CH4 REFORMING
LIQUEFACTION 2nd STAGE
COAL-BITUMEN (HEAVY OIL) SYNCRUDE

Fig. 2 – Block diagram of the ARC two-stage CO/steam – H_2 coal/bitumen process

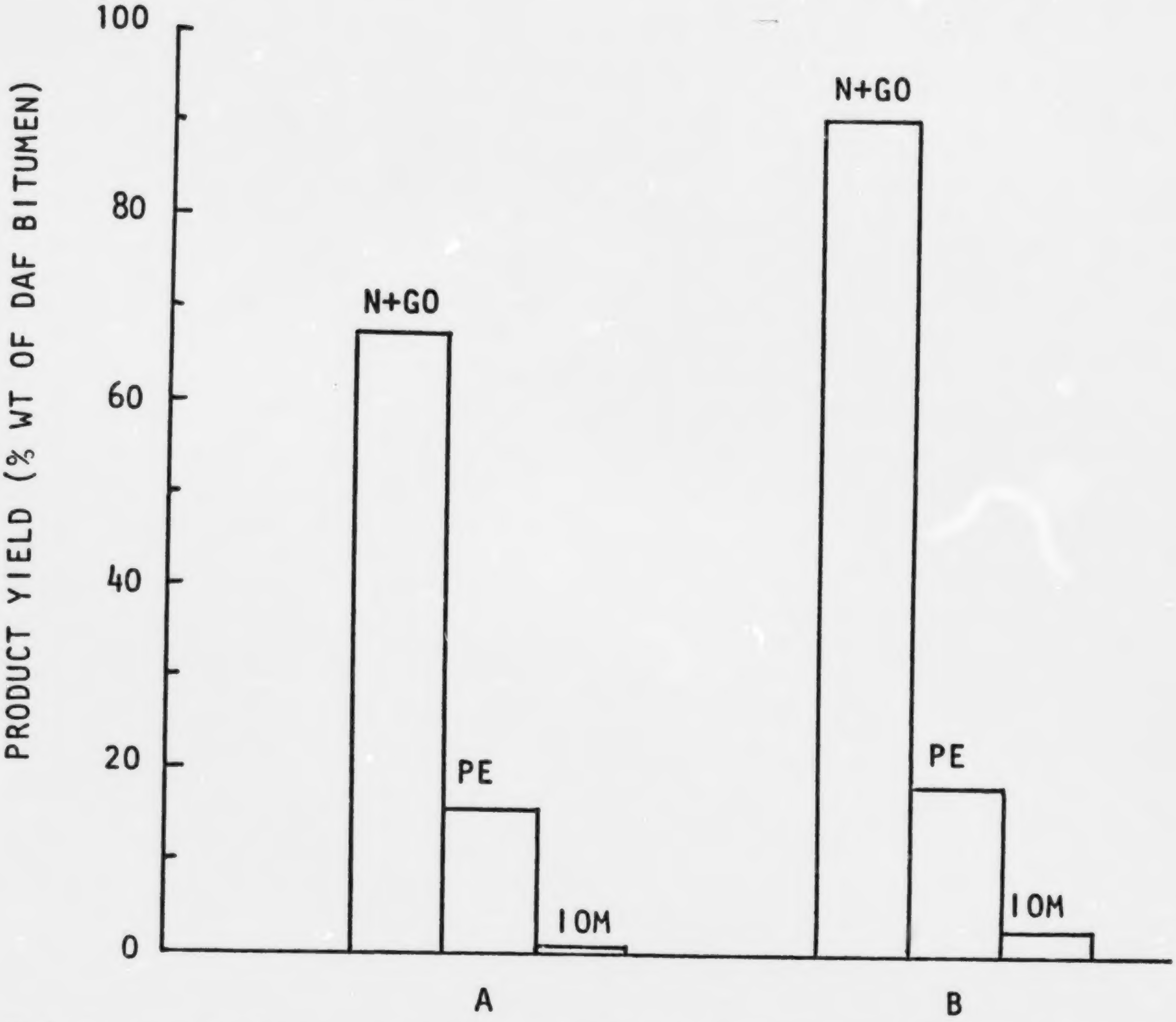

Fig. 3 – The comparison of coprocessing Highvale coal/bitumen blend and bitumen alone in hot charge/discharge unit
A – Bitumen: I Stage – 390°C; II Stage – 457°C
B – Coal/bitumen blend: I Stage – 390°C; II Stage – 464°C

SESSION V: PAPER 21

CANMET COPROCESSING: A STATUS REPORT

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ABSTRACT

CANMET is developing a process to simultaneously liquefy coal and upgrade bitumen, heavy oil or petroleum residues. This coprocessing concept is similar to a direct hydroliquefaction process in which the normal coal-derived recycle oil is replaced with an externally supplied bitumen or other solvent. Alternatively, it can be viewed as an extension of the CANMET hydrocracking process where much greater coal concentrations are employed in the feed. The net result is a single-stage process which combines aspects of both coal liquefaction and heavy oil hydrocracking technologies.

At the Synthetic Fuels Research Laboratory of CANMET a continuous bench-scale coprocessing unit has been used to demonstrate the feasibility of the concept using Forestburg subbituminous C coal from Alberta and Cold Lake vacuum bottoms as solvent. The same coal has also been processed with an anthracene oil solvent to allow direct experimental comparison of product qualities and yields between coprocessing and liquefaction.

The characteristics of coprocessing were investigated by changing the major process variables over wide operating ranges, including the base case of simple hydrocracking of the solvent. A number of significant trends were observed, especially with respect to the effect of coal concentration in the slurry feed. These results are discussed, including the nature of potential coal-solvent synergism during coprocessing.

**denotes speaker*

PRÉSENTATION 21

COTRAITEMENT CANMET: UN RAPPORT D'ÉTAPE

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CANMET, Laboratoires de recherche sur l'énergie

RÉSUMÉ

CANMET procède à la mise au point d'un procédé susceptible de permettre la liquéfaction du charbon tout en améliorant le bitume, le pétrole lourd ou les résidus de pétrole. Ce concept de cotraitement ressemble à un procédé d'hydroliquéfaction directe où le pétrole régulier recyclé tiré du charbon est remplacé par un bitume ou un autre solvant provenant de l'extérieur. On peut également le considérer comme une extension du procédé d'hydrocraquage CANMET, qui permet l'utilisation de concentrations de charbon nettement supérieures dans la charge d'alimentation. Le résultat net prend la forme d'un procédé à étape unique qui combine certains aspects de la technologie de la liquéfaction du charbon et de la technologie de l'hydrocraquage du pétrole lourd.

Au Laboratoire de recherche sur les carburants synthétiques de CANMET, on a utilisé une installation de cotraitement en continu, à l'échelle du banc d'essai, pour démontrer la faisabilité du concept en utilisant du charbon subbitumineux C Forestburg, en provenance de l'Alberta, et des résidus de destillation sous vide de Cold Lake comme solvant. Le même charbon a également été traité avec un solvant de pétrole anthracénique pour permettre une comparaison expérimentale directe des qualités de produit et des rendements fournis par le cotraitement et la liquéfaction.

Les caractéristiques du cotraitement ont été étudiées en modifiant les grandes variables du procédé, sur d'importantes gammes d'exploitation, y compris le cas de base du simple hydrocraquage du solvant. Un certain nombre de tendances significatives ont été observées, tout particulièrement en ce qui concerne l'incidence de la concentration de charbon dans la charge d'alimentation semi-liquide. Ces résultats sont examinés, notamment la nature du potentiel synergétique charbon-solvant durant le cotraitement.

**indique le conférencier*

CANMET COPROCESSING: A STATUS REPORT

INTRODUCTION

The close proximity of large reserves of low-rank coals and bitumens or heavy oils in Canada presents a special upgrading opportunity. CANMET has expended many years of research and development to bring its hydrocracking process to the commercialization stage. A logical extension is to investigate its potential for coprocessing coal and heavy oil resulting in a process having advantages over the individual upgrading of each feedstock. Therefore, a research program was initiated to develop a CANMET coprocessing technology. Autoclave and continuous bench-scale facilities were installed at CANMET's Energy Research Laboratories. Preliminary research begun in the fall of 1981 has demonstrated the feasibility of coprocessing (1-4). Figure 1 shows the research and development plan for the next five years. Currently a 0.5 t/d (4 bbl/day) pilot plant is being constructed to investigate longer term process operability. It is expected to be operational by the beginning of 1986. Consideration is being given to the construction of a 200 bbl/day process development unit flexible enough to run in either the hydrocracking or the coprocessing modes. The CANMET hydrocracking process is being commercialized by Petro-Canada and Partec Lavalin. A 5,000 bbl/day demonstration plant is under construction at Montreal, Quebec. It is expected to be operational by the end of 1985. Operation of this plant in the coprocessing mode is projected for 1990.

When discussing coprocessing, there is a need to know how it compares with the individual upgrading of coal or oil feedstocks. Using results generated from the coprocessing of an Alberta subbituminous coal (Forestburg subbituminous C) and Cold Lake vacuum bottoms a comparison of each process was made. The same experimental unit (1 kg/h bench scale) was used to allow a more representative comparison between hydrocracking of the vacuum bottoms only (based on the CANMET hydrocracking process), liquefaction of the coal (using hydrogenated anthracene oil solvent) and coprocessing.

Also of major importance is the nature or characteristics of coprocessing as a separate processing route. For example, in the published literature there is reference to a *synergism* during coprocessing (5-7). This paper presents an overview of the characteristics of CANMET coprocessing with special emphasis on the effects of coal concentration in the slurry feed and the nature of this synergism.

EXPERIMENTAL

Feedstocks

Forestburg subbituminous C coal from Luscar Ltd. was used for all experiments. The nut-size coal was sent to the Ontario Research Foundation for grinding (with dry ice) to − 74 + 37 µm. Table 1 gives the characteristics of the ground coal.

Cold Lake vacuum bottoms from the Strathcona refinery of Imperial Oil Ltd. were used for the coprocessing and hydrocracking runs. The bottoms are nominally the + 454°C cut. Table 2 gives the characteristics of this feedstock.

For the coal liquefaction experiments, the slurrying solvent was hydrogenated anthracene oil obtained from Crowly Tar Products Inc. It was hydrogenated by the Sandwell Beak Research Group using their process development unit. Table 3 shows the characteristics of the hydrogenated anthracene oil.

Feed slurries were prepared by mixing the desired amounts of coal, and vacuum bottoms or anthracene oil under atmospheric pressure in a stirred feed tank. A disposable catalyst (CANMET additive) was used and the amount of catalyst was kept constant on a moisture- and ash-free (maf) slurry feed basis for all experiments.

Continuous-flow Experiments

Figure 2 shows a schematic diagram of the CANMET continuous-flow coprocessing unit used for this work. The gas feed system consists of two identical pressure and flow controlled lines for hydrogen and carbon monoxide. The slurry feed system consists of a slurry feed tank, recirculation pump and a high-pressure metering pump. The slurry feed tank is mounted on a scale to monitor and record the exact amount of slurry fed to the reactor. The recirculation pump provides additional mixing action and generates the necessary net positive suction head for the metering pump. The four-headed metering piston pump delivers the slurry feed at a preset rate to the reactor. Both the reacting gases and the slurry are fed to the bottom of a 1-L stirred tank reactor. The reactor is fitted with an overflow tube through which the product flows to either an off-specification receiver or a sample receiver. The vapours from either receiver pass through a water-cooled condenser where condensible light ends are separated. The effluent gas then passes through a scrubber and an automatic high-pressure let-down system. The volume of exit gas is metered before it is discharged to vent.

Both the whole slurry product and the light ends are discharged directly into pressurized vessels which are weighed before depressurization and product workup.

Product Workup

Samples of the outlet gas were analyzed by gas chromatography to determine hydrogen, hydrocarbon gases (C_1-C_4), hydrogen sulphide, and carbon oxides contents. Water was separated from the light ends by freezing and the organic light ends were then mixed with the whole slurry product. A sample of this mixture was distilled using a spinning band distillation unit into distillate (−525°C product) and residue (+525°C product) by a combination of atmospheric and vacuum distillation. The distillate was analyzed for:

- specific gravity by PARR densimeter;
- boiling range by g.c. simulated distillation according to ASTM D2287;
- hydrogen, carbon and nitrogen using a CHN 240 Perkin Elmer analyzer. Sulphur was determined by X-ray fluorescence, Tech. Chemical Analyzer Model 100;
- PONA analysis by GC-MS using a GC/MS Finnigan 4000 instrument with INCOS data system;
- aromaticity by H-NMR using a Varian CFT-20 pulse Fourier Transform instrument (Brown Ladner treatment).

The residue was analyzed to obtain:

- elemental composition; C, H, N, S and O contents
- the content of oils, asphaltenes and preasphaltenes by sequential soxhlet extraction
- ash content by ASTM D-482
- metal content by Jarrell Ash Model 850AA spectrometer.

The results presented were obtained from a total of 30 experimental runs. In 26 runs, the material balance was better than ±5% and in 4 runs it was better than ±7%.

COAL LIQUEFACTION, COPROCESSING AND HYDROCRACKING AS UPGRADING ALTERNATIVES

In comparing the alternative processes, it is necessary to define the basis for the comparison and to note terms and definitions that do not coincide with more common usage in coal liquefaction or hydrocracking technology. Figure 3 presents a schematic diagram of the basic process flows used for this comparison. Hydrocracking is represented by the coprocessing schematic less the separate coal feed. However, a small amount of coal is added to the bitumen as a processing additive in the CANMET hydrocracking process, which was selected for this comparison. The bench-scale continuous-flow experimental unit was used in different operating modes at the same process conditions. These conditions were close to the optimum for coprocessing. No attempt was made to optimize the liquefaction or hydrocracking processes since the basis for the comparison was to fix the operating conditions. Figure 3 shows a basic advantage of coprocessing over liquefaction in that no recycle oil stream is needed.

Since the comparison is basically between three stirred tank reactors of equal volume operating at the same space velocity, all calculated process data are referenced to each reactor input on a maf slurry feed basis. This is different from standard coal liquefaction practice where the net maf coal input is usually used as a basis for process comparisons. Also, when comparing pitch conversions between coprocessing and hydrocracking it should be noted that maf coal in the feed is considered as pitch (i.e., +525°C ash-free material) for the liquefaction and coprocessing cases. Normally, the CANMET hydrocracking process operates in the +85 wt % pitch conversion range. The process conditions chosen for this comparison resulted in a much lower pitch conversion.

Process Comparison

Table 4 compares the experimental results from each process on the basis of 100 g maf slurry fed to the reactor. The liquefaction yields were calculated by subtracting the necessary recycle oil stream from the total oil yield (less the naphtha fraction), assuming that the hydrogenated anthracene oil solvent in this one-pass operation behaved as a steady-state recycle solvent. On this basis coprocessing results in about 4-5 times more total oil yield (distillate + residual oil) than liquefaction but slightly less than hydrocracking. Because of the different solvents used in liquefaction and coprocessing, it is not surprising to see a much larger residue yield (+525°C ash-free product) for coprocessing.

Under more severe operating conditions, the residue yield for hydrocracking can be reduced with corresponding increases in oil and gas yields. The higher gas yield for coprocessing, compared with hydrocracking, is probably due to a higher concentration of catalytically active mineral matter in the slurry feed in the coprocessing mode.

Similar coal conversions for liquefaction and coprocessing indicate that Cold Lake vacuum bottoms perform as well as the hydrogenated anthracene oil solvent, at least under the process conditions used in this comparison. Other work has shown Cold Lake vacuum bottoms to be as good as or better hydrogen donors than tetralin in the absence of gaseous hydrogen (8).

The hydrogen consumption values show the expected trend, with coprocessing slightly higher than hydrocracking due to the presence of much more coal. For liquefaction, a hydrogen consumption of 2.7 wt % on maf slurry feed (8.2 wt % on maf coal) was measured. This was higher than would be expected for a direct hydroliquefaction process with a total oil yield of 16.5 wt % on maf slurry feed (50 wt % on maf coal). However, the trend shown for hydrogen utilization efficiency from liquefaction, to coprocessing, to hydrocracking is typical. In fact, the hydrogen utilization efficiency for CANMET coprocessing is higher than that reported for most integrated two-stage coal liquefaction processes (9-11).

Distillate Yields and Characteristics

Total distillate yields for the three processes and their naphtha, light gas oil (LGO) and heavy gas oil (HGO) fractions are shown in Figure 4. Overall, there is a decreasing trend in distillate yields from hydrocracking, to coprocessing, to liquefaction. As a percentage of the total distillate yield, there is little difference in the naphtha, LGO and HGO fractions when comparing hydrocracking with coprocessing. However, coal liquefaction shows a smaller LGO yield and larger HGO yield as a percentage of the total distillate yield. This is probably due to the conversion of most of the coal into high molecular weight products with little upgrading of the hydrogenated anthracene oil solvent.

Because of the use of a hydrogenated anthracene oil solvent and a single-pass operation, care must be taken in making yield comparisons with liquefaction. However, the total distillate yield for liquefaction of about 14.5 wt % (44.0 wt % on maf coal basis) is in the range reported for single-stage direct hydroliquefaction processes of this type. The overall trends shown in Figure 4 are correct, but the absolute values shown for the distillate fraction yields for liquefaction would have to be verified by running long enough to generate a true steady-state recycle solvent and products.

Figure 5 shows some of the characteristics of the whole distillate (IBP to 525°C) from each process. Because of the nature of single-pass operation, only the trends for the liquefaction data should be considered and not the absolute values. The trends in aromaticity, H/C atomic ratio and sulphur content are a strong function of the nature of the slurry feedstock in each case. Using H/C atomic ratio change between feedstock and distillate as an indication of hydrogenation shows a 36% increase for coprocessing versus 18% for hydrocracking and only 7% for liquefaction. The higher value for coprocessing could be due to a slight catalytic effect of the coal mineral matter. Sulphur removals (to gases plus residue) for hydrocracking and coprocessing are equal at about 75 wt %. For liquefaction the distillate sulphur content is much lower because of the low sulphur content of the starting feedstock (0.17 wt %). As expected, aromaticities are higher for liquefaction due to the nature of the anthracene oil solvent employed.

Residue Yields

Figure 6 shows a comparison of the residue yields for the three processes. Residual oil values follow the expected trend based on the pitch or residue contents of the feedstocks. However, the preasphaltenes' yield for hydrocracking is significantly low, although the sum of asphaltenes plus preasphaltenes for coprocessing and hydrocracking is almost equal. Again, this is due to the nature of the feedstocks. Vacuum bottoms contain very few preasphaltenes. In coprocessing, the liquefaction of coal through the preasphaltenes-asphaltenes route would result in higher preasphaltenes' content, primarily derived from the coal portion of the feedstock. Because of the presence of large amounts of coal during coprocessing and liquefaction, much larger amounts of THF insolubles in the residues can be expected compared with hydrocracking. However, coprocessing does not generate significantly larger amounts of THF insolubles compared with liquefaction. Also, the ash content of the residue is about 11% for coprocessing versus 27% for liquefaction.

CANMET COPROCESSING CHARACTERISTICS

The coprocessing of Forestburg subbituminous C coal and Cold Lake vacuum bottoms was investigated over a wide range of operating conditions. A series of experiments was carried out using a slurry of the coal and the heavy oil with a fixed coal concentration. The gross performance was examined at various processing severities.

Yields

Figure 7 shows the distillate (C_5 to −525°C product), residue (+525°C product) and hydrocarbon gas yields as a function of pitch conversion. Distillate yields as high as 75.4 wt % (based on maf slurry feed) were obtained at a pitch conversion of 87.4 wt %.* The linear increase of distillate yield is accompanied by an equivalent linear decrease in the residue yield. The increase in the gas yield with pitch conversion is relatively small, indicating that at the highest level of severity most of the hydrocracking resulted in the production of liquid rather than gaseous products.

Figure 8 shows the yields of distillate fractions as a function of pitch conversion. The overall increase in distillate yield at higher severity is due to an increase of light and middle distillates, since the heavy gas oil II fraction decreases at higher severity. Control of the product slate by controlling the severity of coprocessing seems feasible if the market value of the desired products will tolerate a slight penalty in the overall yield obtained at lower severities.

Distillate Characteristics

Figure 9 shows the specific gravity and H/C atomic ratio of the whole distillate product as a function of pitch conversion. A very distinct drop in the specific gravity with increasing pitch conversion can be observed. The specific gravity changed from 0.953 to 0.893 which corresponds to a 10 unit increase in the °API gravity over the range of pitch conversions tested. The decrease in the specific gravity of the distillate product relative to that of the feed ranges from 0.085 to 0.145. This corresponds to an °API uplift in the range of 12 to 22 °API. Two-stage coprocessing was reported to give °API uplifts in the range of 6 to 12.4 °API (6). Despite the scatter in the H/C atomic ratio data, linear regression shows an overall increase, as expected, from the drop in the specific gravity.

Figure 10 shows the distillate sulphur content. Comparing the sulphur content of the slurry feed with that of the distillate shows that desulphurization occurs to a significant extent even at low severity. The sulphur removal continues to increase at higher severities.

Coal Conversion

Coal conversions from 51 wt % to 87 wt % were obtained depending on the severity. This level of conversion is similar to that obtained using classical coal liquefaction solvents. It was observed that pitch conversion was more sensitive to changes in temperature and space velocity than coal conversion. Figure 11 shows that the primary dissolution of coal during coprocessing can be accomplished to a large extent at low temperatures. The activation energy for secondary upgrading is higher, therefore higher temperatures are required for significant secondary upgrading to take place. Figure 12 shows the effect of space velocity on coal conversion and pitch conversion. The less significant effect of space velocity on coal conversion compared with pitch conversion is not unexpected. It is known from short contact time studies in coal liquefaction that high coal conversions can be obtained in the first few minutes of reaction (12). This would support a two-stage approach for coprocessing where most of the primary coal dissolution could be accomplished in a separate reactor at high space velocity and where secondary upgrading would be allowed to take place in a second-stage reactor at lower space velocity and using appropriate catalysts. Optimization of the overall liquid yields would be accomplished by controlling the temperatures and the space velocities of both reactors. Preliminary bench-scale tests at CANMET indicate that the two-stage approach is feasible, although much more research is needed to determine overall process performance improvement over the single-stage approach (13).

Yields of Residue Components

Soxhlet extractions were carried out on all the residue products in order to estimate the individual yields of residual oils, asphaltenes, preasphaltenes and THF insolubles. Figure 13 shows the variation of the yields of each component with process severity. At high pitch conversions, the sum of yields of residue components, i.e., the overall residue yield based on maf slurry feed, is much lower than the original coal concentration in the slurry feed. This provides direct evidence that the coal portion of the feedstock contributes to the distillate product. Figure 13 demonstrates that at all levels of pitch conversion, residual oils constitute a major portion of the nondistillate product. It also indicates that preasphaltenes do not build up to a significant extent with increasing severity. Because of their high reactivity, preasphaltenes quickly react progressively to form asphaltenes or oils. The THF insolubles' depletion and that of the asphaltenes are equivalent. This suggests that the sensitivity of asphaltene and coal conversions to process severity is similar.

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* Pitch conversion = $\left[1 - \dfrac{+525^\circ\text{C fraction in product, including coal}}{+525^\circ\text{C fraction in feed, including coal}} \right] \times 100$

Coprocessing Using Synthesis Gas

The same feedstock at the same coal concentration was tested using synthesis gas in place of hydrogen at a CO/H_2 molar ratio of 1:2. It was found that the distillate, residue and gas yields using synthesis gas were identical to those using hydrogen (14). Also, coal and pitch conversions were similar for both reducing atmospheres. A significant difference, however, was observed in the hydrogen consumption. Figure 14 shows the hydrogen equivalent consumption in both atmospheres as a function of pitch conversion. For synthesis gas, hydrogen equivalent consumption is calculated taking into account the hydrogen generated from carbon monoxide through the water-gas shift reaction. Under low severity conditions significantly lower hydrogen consumption is observed for synthesis gas. This difference appears to diminish at higher pitch conversions.

Another distinguishing feature associated with using synthesis gas is the product slate. Figure 15 shows the yields of distillate fractions using synthesis gas. A comparison of Figures 8 and 15 indicates that the relative yields of distillate fractions are different for synthesis gas compared with hydrogen. At high severity, synthesis gas tends to produce more middle distillate and less naphtha. This trend is reversed at low severity. The simulated distillation data shown in Figure 16 support this statement. The curves for distillates obtained at medium severity coincide. Examination of the specific gravity and the H/C atomic ratio of the distillates also supports this observation.

EFFECT OF COAL CONCENTRATION ON PROCESS PERFORMANCE

To assess coprocessing as an upgrading technology, it is important to investigate the effect of increasing coal concentration in the slurry feed. In this section a technical assessment provides some insight into the effect of coal concentration on the yields and qualities of the products. However, an economic evaluation is also needed to complement the technical assessment. CANMET is therefore planning a separate study for the economic assessment of coprocessing versus hydrocracking.

Distillate Yields and Synergism

A number of reports in the literature refer to a synergism during coprocessing (5-7). However, careful examination reveals that the definition of this synergism is somewhat arbitrary and that the comparisons claiming the effect are not necessarily uniform. There can be a synergism related to process operability or some other non-quantitative process variable. However, for CANMET coprocessing, it is felt that the best definition from a quantitative process point of view should be based on distillate yield using the same basis for comparing different processes, i.e., distillate yield based on a wt % maf slurry feed basis. To investigate the potential synergism during CANMET coprocessing, distillate yields for 11 levels of maf coal concentration in the slurry feed were measured. All tests were carried out under identical operating conditions. Figure 17 shows the variation of the distillate yield with increasing coal concentration. There is a definite true synergism at low coal concentrations. In this region, increases in the distillate yield of up to 9 wt % were found over operating with no coal. For the range of coal concentrations of interest in coprocessing, distillate yields remain constant and equal to those for the no coal case and start to drop for higher coal concentrations. Therefore, over the range of coal concentrations of most interest, there is no observed synergism for coprocessing compared with hydrocracking of the solvent only based on distillate yield. However, there was a marked improvement in the operability of the process for coal concentrations in this range compared with the no coal case. One goal of CANMET's research program is to broaden the distillate yield peak so that a true process synergism can be obtained over a wider range of coal concentrations.

For comparison, the dashed line in Figure 17 is a tie-line connecting the yield obtained for the no coal case (on a *maf feed basis*) with the 100% coal case (coal liquefaction on a *maf coal feed basis*). This type of tie-line has been used to indicate the expected distillate yields from coprocessing, assuming additive behaviour of the mixtures (5). Except at the highest coal concentrations shown, CANMET coprocessing results in distillate yields above the tie-line and could therefore be credited as showing a synergism. However, over the range of coal concentrations where a plateau in distillate yield was observed, there may also be a synergism in terms of hydrogen addition. As the coal concentration was increased in the feedstock, the H/C atomic ratio of the feed became lower. More hydrogen addition would be required to achieve the same distillate yield (and quality as indicated in the distillate characteristics section) from a lower quality feedstock.

Residue and Gas Yields

Figure 18 shows corresponding residue and gas yields as a function of coal concentration. As expected, the residue yields result in a rough mirror image of the distillate yields, since the hydrocarbon gas production remains relatively constant with increasing coal concentration. Since the catalyst concentration was fixed on a maf slurry feed basis, the increase in residue (and decrease in distillate) at higher coal concentrations may be related to the need for higher catalyst concentrations at these levels (i.e., it may be preferable to fix the catalyst concentration on a maf coal basis).

Distillate Characteristics

Over the range of coal concentrations studied, the distillate quality remained basically constant. Figure 19 shows specific gravity, aromaticity and H/C atomic ratio. There is only a marginal decrease in the H/C atomic ratio and consequently a slight increase in the aromaticity of the distillate. Detailed compound-type analysis showed that the percentage of paraffinic, olefinic, aromatic and polar compounds in the distillate did not change significantly with the addition of coal to the feedstock (15).

Figure 20 shows the sulphur content of both the distillate and the slurry feed as a function of coal concentration. An overall decrease in the sulphur content was observed with increasing coal concentration. However, this is primarily due to the feedstock progressively containing less sulphur as more coal replaces the vacuum bottoms.

Coal Conversion

Figure 21 presents the coal conversion data. Despite some scatter, a trend is shown as a decrease followed by a gentle increase in the coal conversion. We have no explanation for the initial decrease in coal conversion. The subsequent increase, however, indicates that at all coal concentrations, the solvent-to-coal ratio used was not a limiting factor. More coal was converted as more coal was introduced. Also, the slight increase in coal conversion at higher levels of coal concentration may be attributed to larger amounts of mineral matter which can have a slight catalytic effect.

CONCLUSIONS

The feasibility of coprocessing Forestburg subbituminous C coal and Cold Lake vacuum bottoms was demonstrated. Coprocessing of this feedstock was compared with coal liquefaction and hydrocracking under identical operating conditions. This comparison showed:

1. The total oil yield for coprocessing was 4.6 times greater than that for coal liquefaction and 7% less than that for hydrocracking.
2. Similar coal conversions were obtained for coprocessing and coal liquefaction.
3. The hydrogen consumption for coprocessing was 50% higher compared with coal liquefaction and 21% higher compared with hydrocracking.
4. The hydrogen utilization efficiency for coprocessing was 2.6 times as much as that for coal liquefaction and 30% lower than that for hydrocracking.
5. The hydrogen addition was 36% for coprocessing, 18% for hydrocracking and 7% for coal liquefaction.
6. The distillate obtained from coprocessing had lower specific gravity, higher H/C atomic ratio, lower aromaticity and higher sulphur content, compared with the distillate obtained from coal liquefaction.

The coprocessing of Forestburg coal and Cold Lake vacuum bottoms was tested over a range of operating conditions. Examination of product yields and qualities showed:

- Distillate, residue and hydrocarbon gas yields changed linearly with pitch conversion.
- The increase in the overall distillate yield with pitch conversion was mainly due to an increase in middle distillate yield.
- At a typical pitch conversion the H/C atomic ratio of the distillate product was 1.58, the API gravity was 25.7° and the sulphur content 1.56 wt %.
- The level of coal conversion was similar to that reported for good coal liquefaction solvents.
- Coal conversion was more sensitive to temperature variations than to space velocity variations.
- The coal portion of the feedstock contributes to the distillate product yield, particularly at high severity.
- Using synthesis gas in place of hydrogen reduces the hydrogen consumption at low severities and enhances the production of middle distillates at high severities.

The process performance was studied over a range of coal concentrations and revealed the following:

a. At very low coal concentrations, the distillate yields were remarkably enhanced compared with the no coal case.

b. Over a considerable range of coal concentrations the distillate yield was constant and equal to that obtained in the no coal case.

c. Over a large range of coal concentrations, synergism was observed in terms of process operability and hydrogen addition rather than distillate yields.

d. Above a critical level of coal concentration the distillate yields decrease significantly.

e. Over the range of coal concentrations tested, the distillate quality was essentially constant.

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TABLES

Table 1 – Characteristics of Forestburg subbituminous C coal

Proximate analysis "as received", wt %		
Moisture	19.17	
Ash	7.68	
Volatile matter	34.00	
Fixed carbon	39.15	
Ultimate analysis "dry basis", wt %		
Carbon	64.04	
Hydrogen	3.87	
Sulphur	0.53	
Nitrogen	1.65	
Ash	9.50	
Oxygen by difference	20.41	
Metal content		
Fe	2379	ppm
Ni	18	ppm
V	trace	
Calorific value	4933	cal/g
	8879	Btu/lb
Petrographic analysis*		
Mean R_o (random)	0.42	
Vitrinite	92.2	vol %
Liptinite	2.6	vol %
Inertinite	3.1	vol %
Mineral matter	2.1	vol %

* *Supplied by the Energy Research Unit, University of Regina*

Table 2 – Characteristics of Cold Lake vacuum bottoms

General		
Specific gravity 15/15°C	1.038	wt %
Conradson carbon residue	17.1	wt %
Asphaltenes	23.48	wt %
Preasphaltenes	0.2	wt %
Aromaticity (^{1}H NMR)	34.5	%
Viscosity at 80°C	249.12	poise
100°C	39.40	"
110°C	21.59	"
Distillation (spinning band method)		
IBP	420	°C
Distillate (−525°C)	16.75	wt %
Residue (+525°C)	83.25	wt %
Elemental analysis, wt %		
Carbon	78.6	
Hydrogen	9.3	
Sulphur	5.5	
Nitrogen	0.6	
Ash	0.0	
Oxygen by difference	5.9	
Metal content ppm		
Ni	93	
V	235	
Fe	18	

Table 3 – Characteristics of hydrogenated anthracene oil

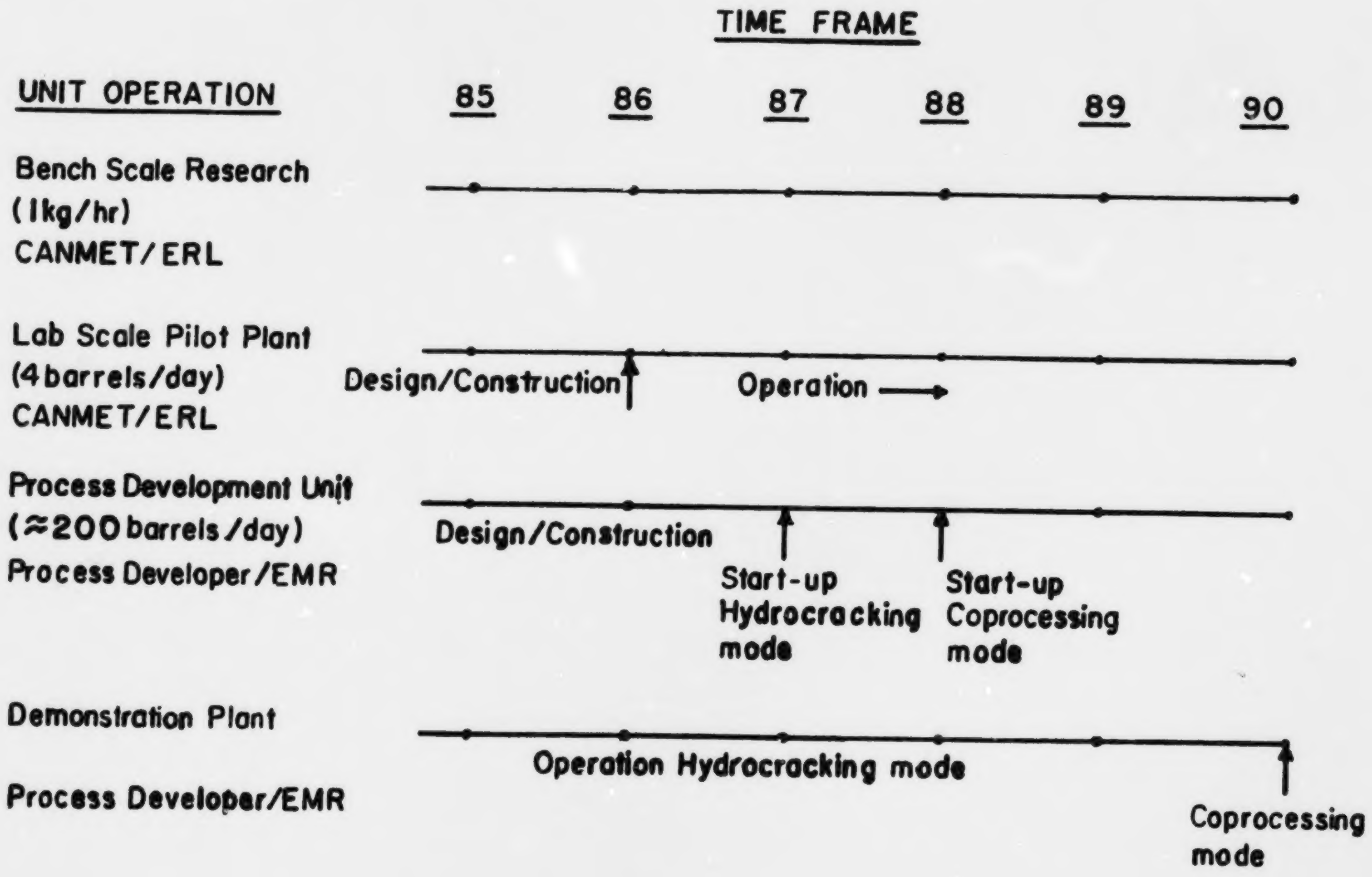
General	
Specific gravity 15/15°C	1.08
Viscosity at 15°C	0.205 poise
at 25°C	0.146 poise
Aromaticity	81.01 %
Distillation	
IBP	243°C
50 vol % off at	308°C
FBP	376°C
Elemental analysis, wt %	
Carbon	91.73
Hydrogen	6.45
Nitrogen	0.56
Sulphur	0.17
Oxygen	1.02

Table 4 – Comparison of processes

Basis: g/100 maf slurry feed

	Liquefaction	Coprocessing	Hydrocracking
Conditions			
Coal (maf)			
Concentration	33	30	—
Temperature	←	Same	→
Pressure		"	
Space velocity		"	
H_2 feed rate		"	
Solvent	Anthracene oil	Vacuum bottoms	Vacuum bottoms
Yields			
Gases (C_1-C_4)	1.3	5.4	3.8
Total oil	16.5	75.9	81.9
Residue	13.2	29.6	22.5
Conversions			
Coal (wt %)	85.6	83.9	—
Pitch (wt %)	57.5	66.5	72.2
Hydrogen			
Consumption	2.7	4.0	3.3
Utilization			
Efficiency (g dist./gH_2)	6.0	15.5	22.2

FIGURES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UNIT OPERATION
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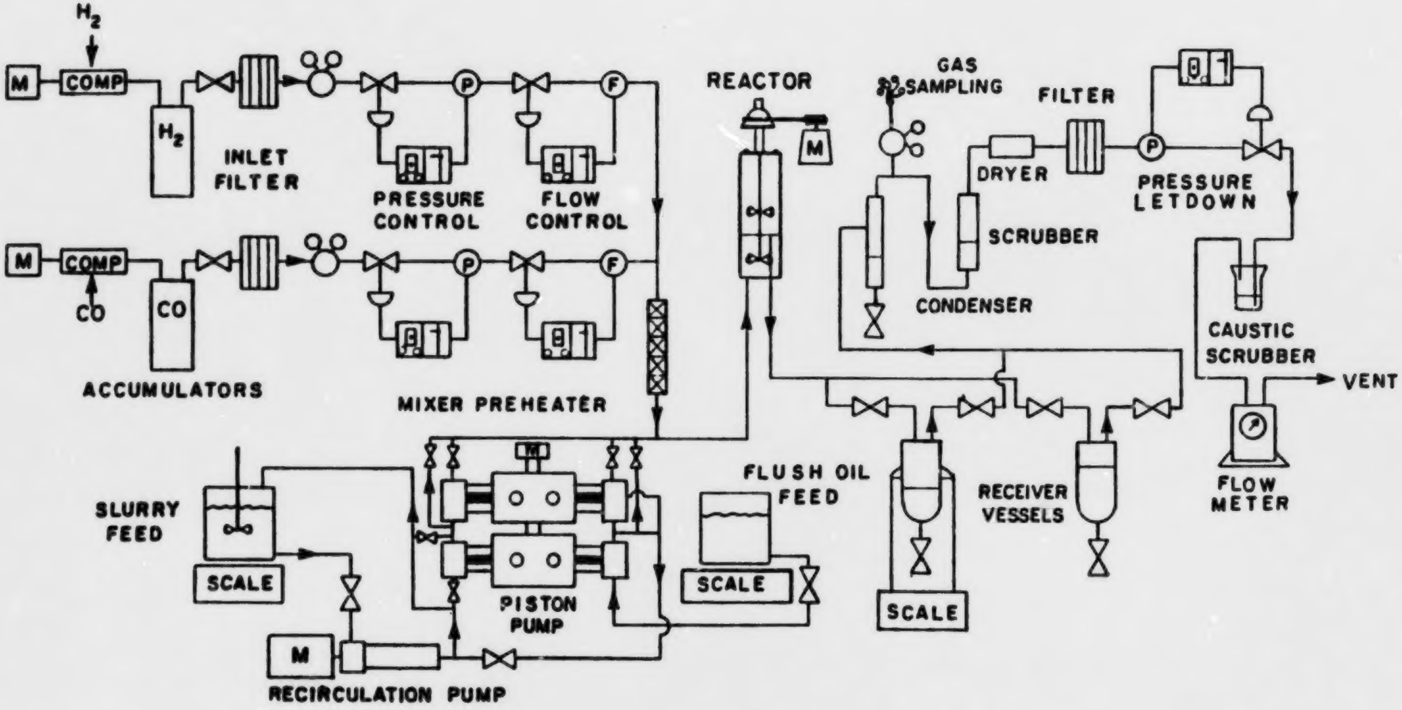
86
87
88
89
90
Bench Scale Research
(1kg/hr)
CANMET/ERL
Lab Scale Pilot Plant
(4 barrels/day)
CANMET/ERL
Design/Construction
Operation
Process Development Unit
(≈200 barrels/day)
Process Developer/EMR
Design/Construction
Start-up Hydrocracking mode
Start-up Coprocessing mode
Demonstration Plant
Process Developer/EMR
Operation Hydrocracking mode
Coprocessing mode

Fig. 1 – Research and development plan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SLURRY FEED
SCALE
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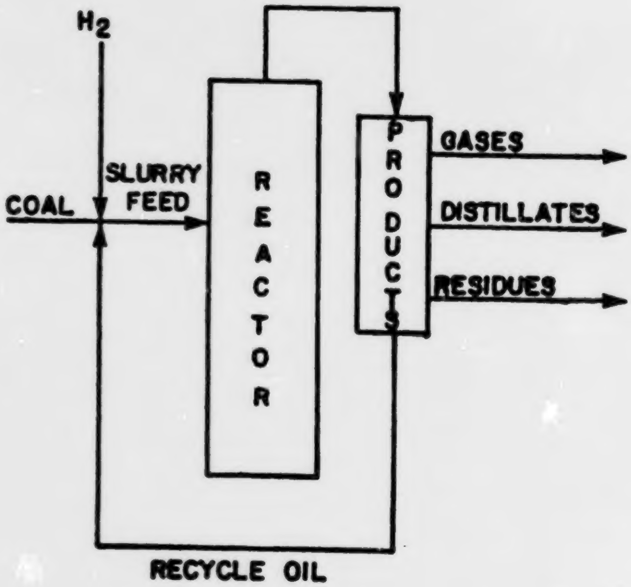
RECIRCULATION PUMP
PISTON PUMP
FLUSH OIL FEED
SCALE
REACTOR
M
GAS SAMPLING
CONDENSER
DRYER
SCRUBBER
FILTER
PRESSURE LETDOWN
CAUSTIC SCRUBBER
VENT
FLOW METER
RECEIVER VESSELS
SCALE

Fig. 2 – CANMET bench-scale coprocessing unit

LIQUEFACTION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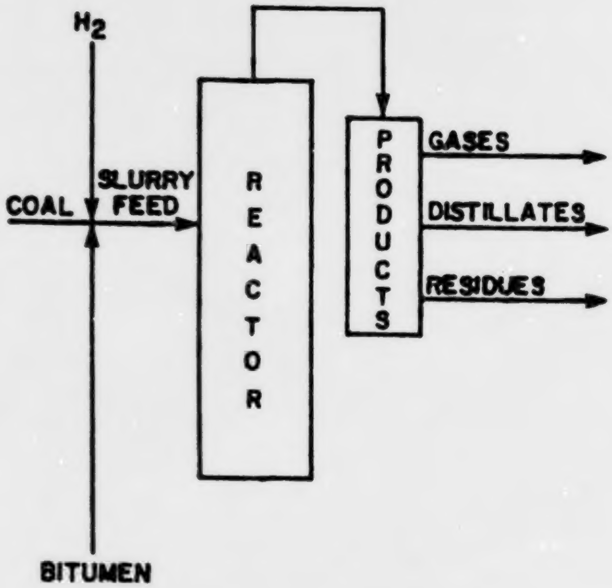
RESIDUES
RECYCLE OIL

COPROCESSING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REACTOR
PRODUCTS
GASES
DISTILLATES
RESIDUES
BITUMEN

Fig. 3 – Process schematics

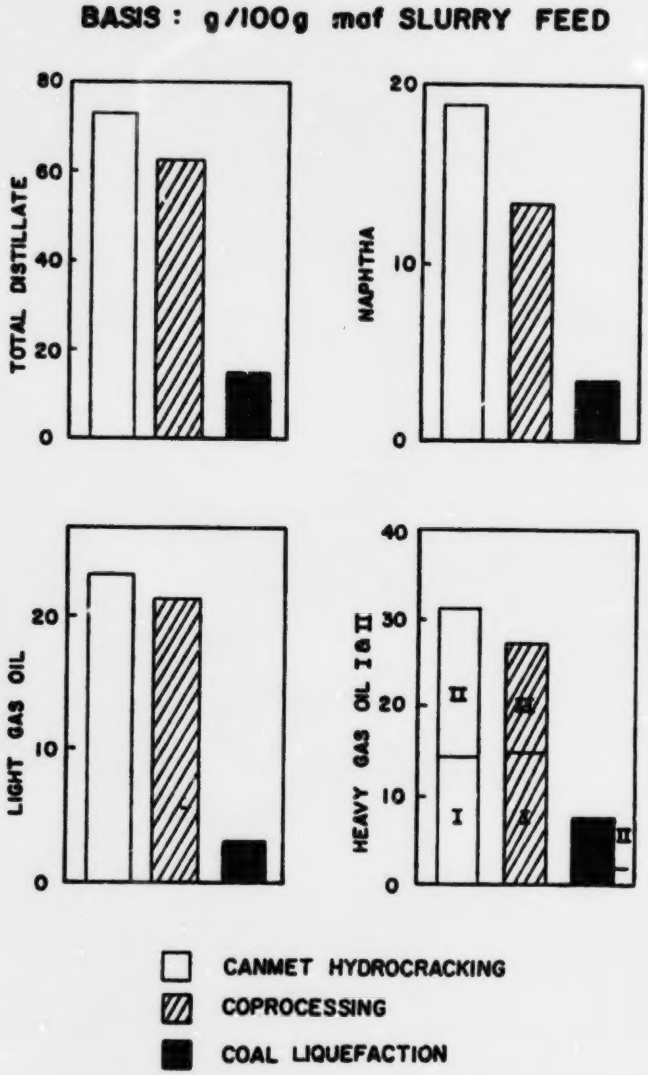

Fig. 4 – Comparison of distillate yields

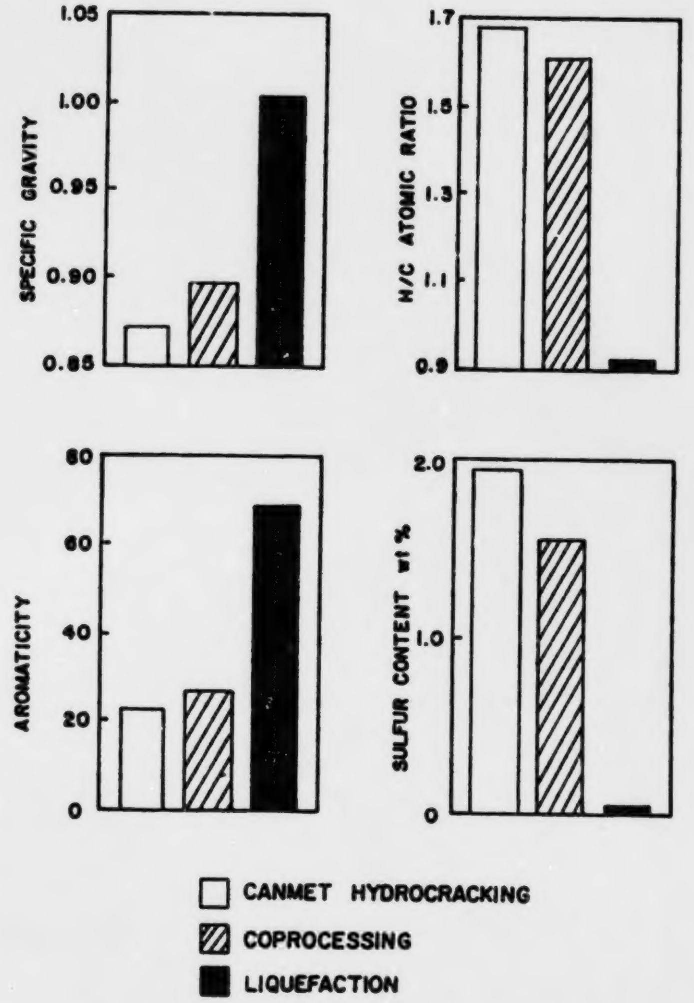

Fig. 5 – Comparison of distillate characteristics

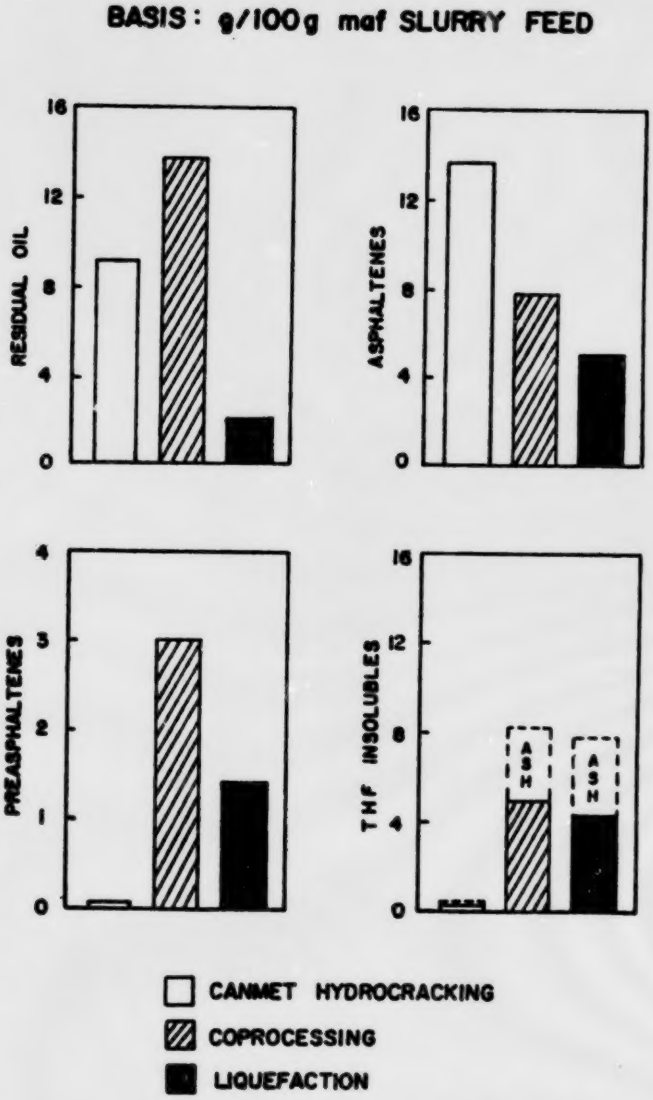

Fig. 6 – Comparison of residue yields

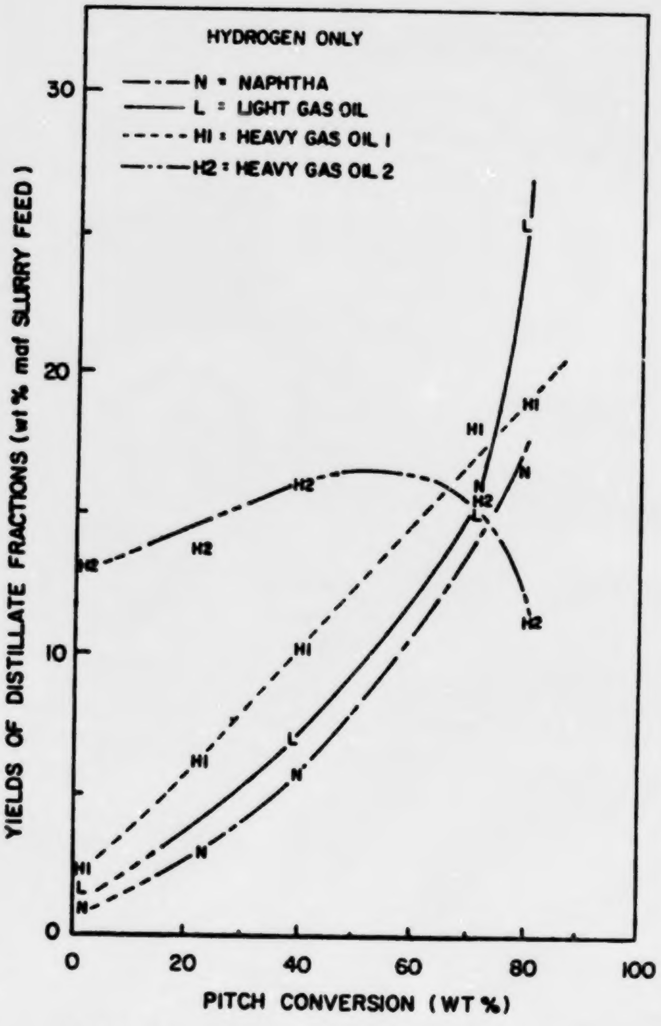

Fig. 7 – Coprocessing yields as a function of severity

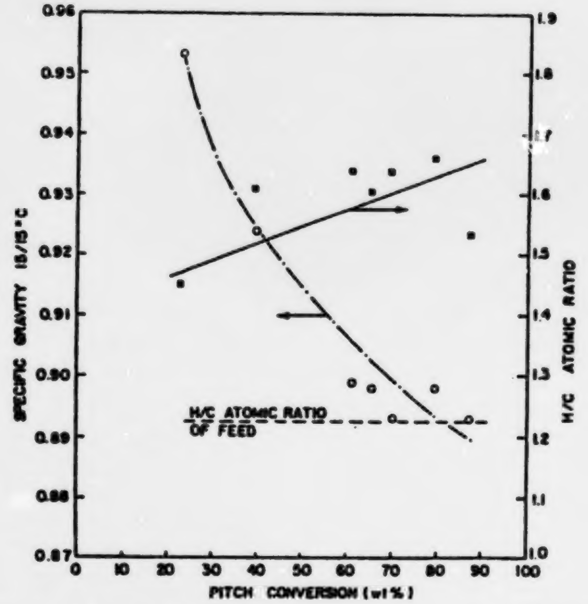

Fig. 8 – Yields of distillate fractions as a function of severity

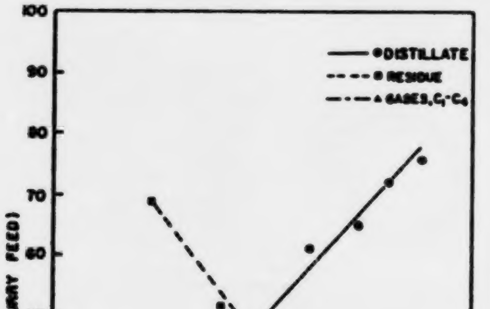

Fig. 9 – Distillate characteristics as a function of severity

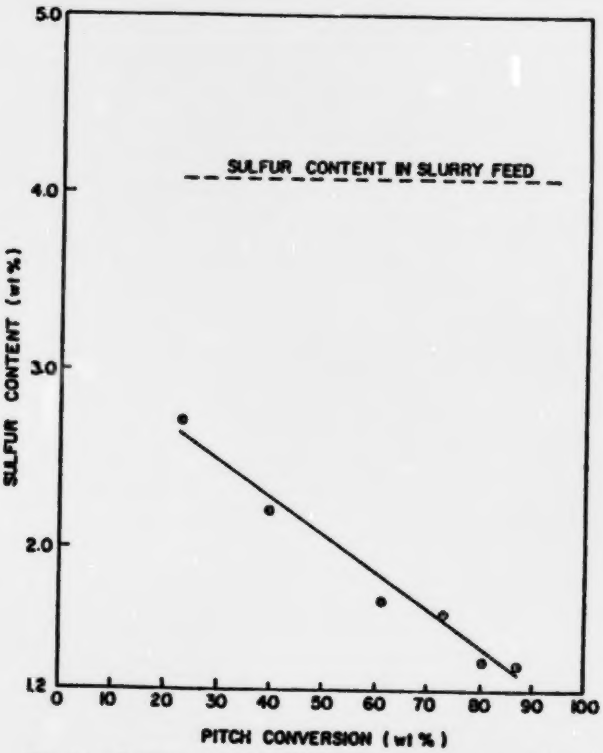

Fig. 10 – Sulphur in distillate as a function of severity

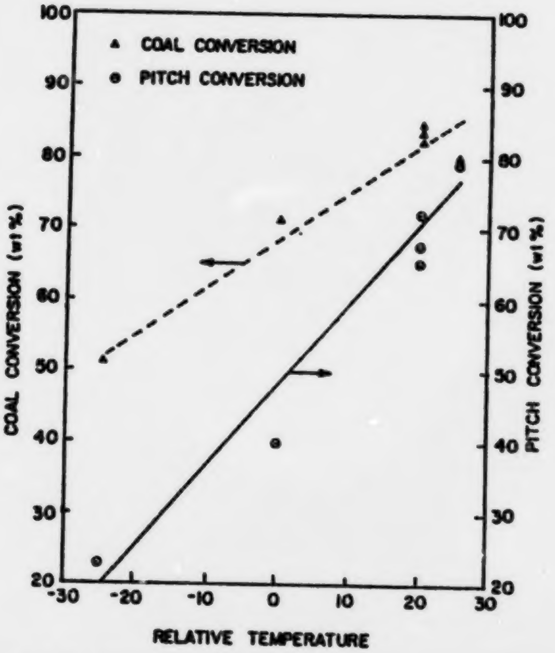

Fig. 11 – Coal and pitch conversion vs temperature

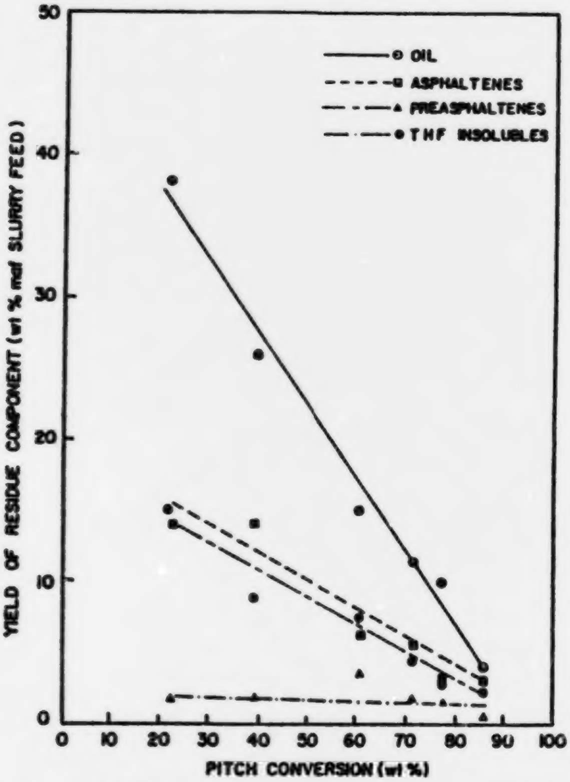

Fig. 12 – Coal and pitch conversion vs space velocity

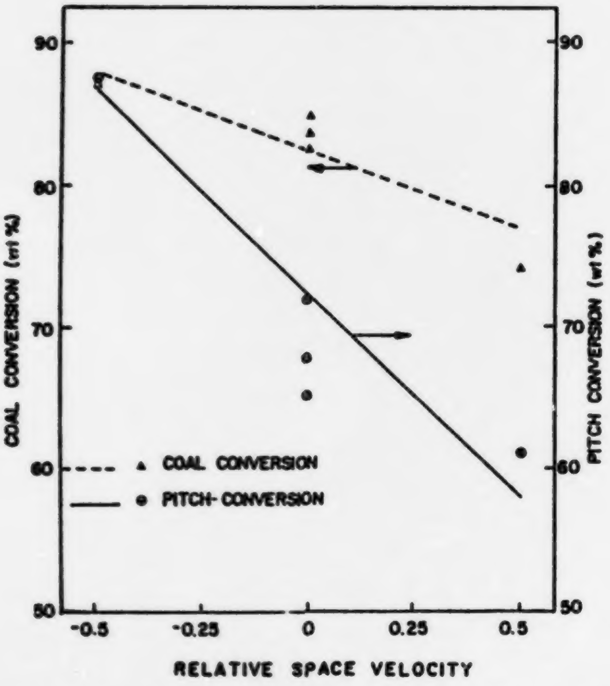

Fig. 13 – Residue characteristics as a function of severity

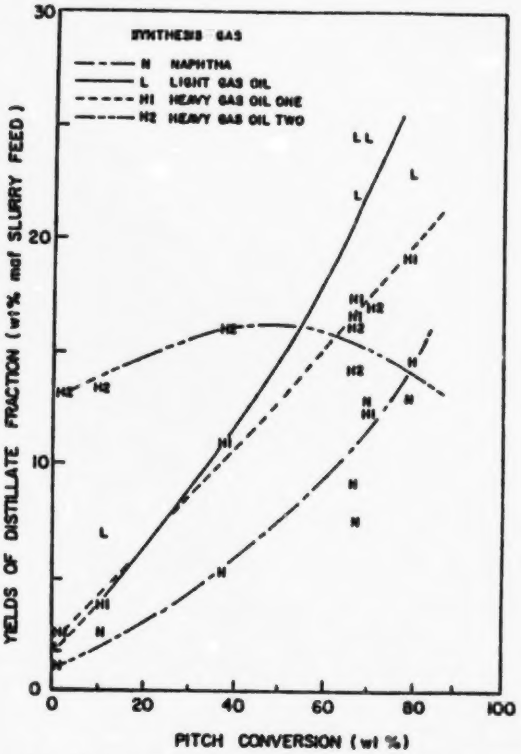

Fig. 14 – Hydrogen consumption as a function of severity

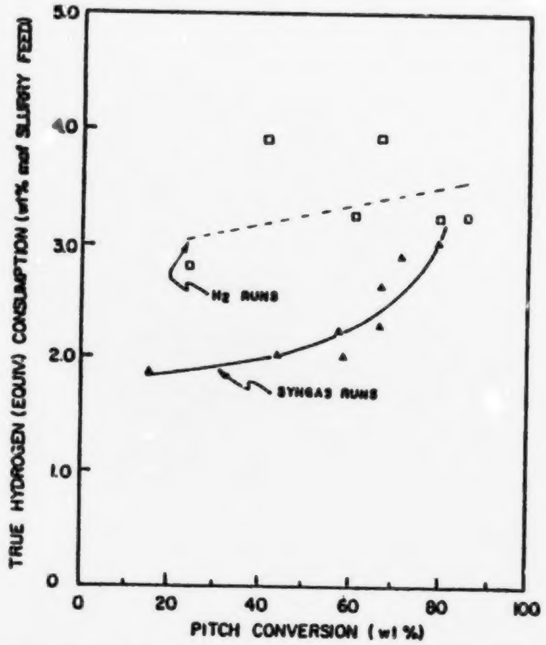

Fig. 15 – Yields of distillate fractions as a function of severity – synthesis gas

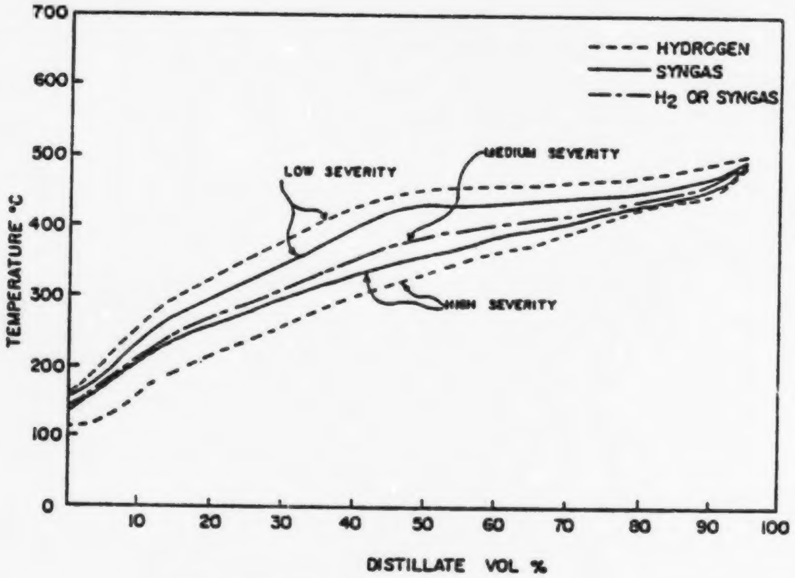

Fig. 16 – Simulated distillation curves

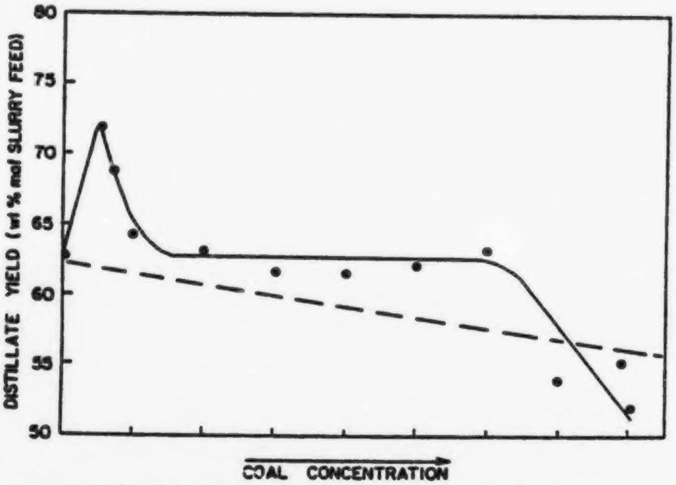

Fig. 17 – Effect of feed coal concentration on distillate yields

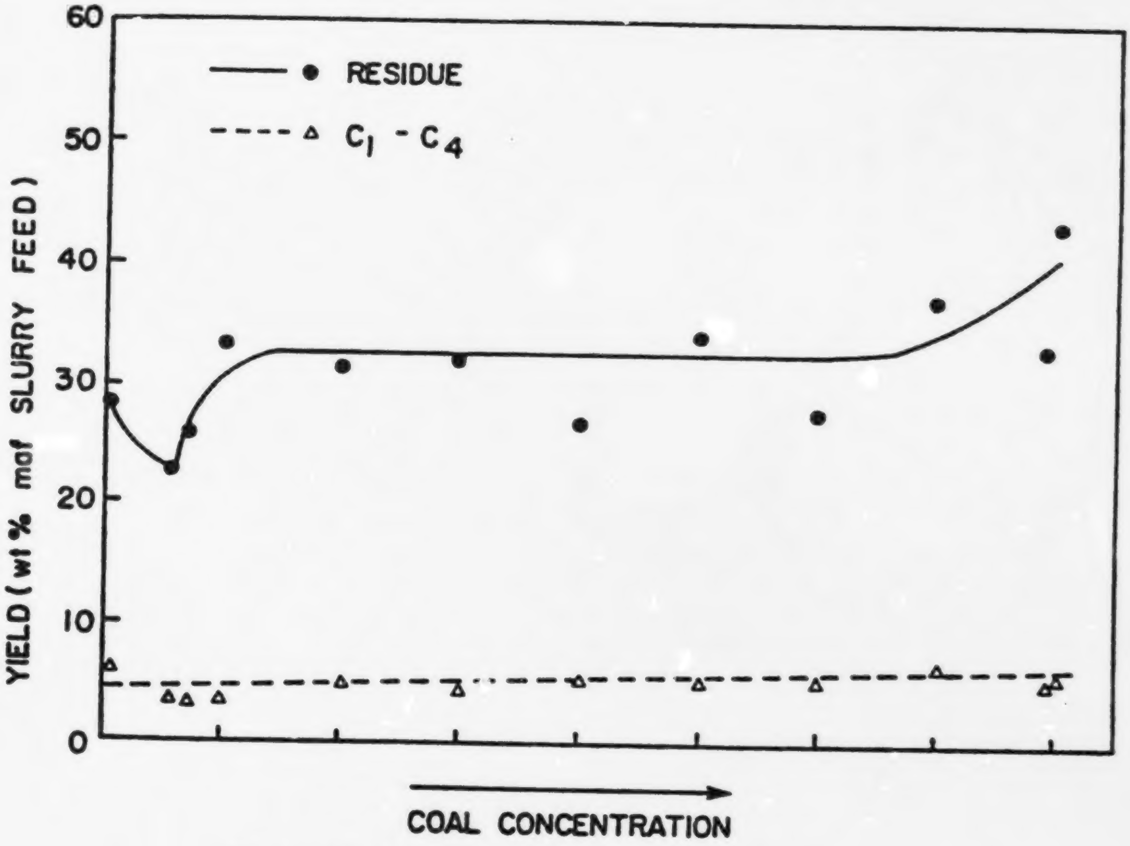

Fig. 18 – Residue and gas yields as a function of coal concentration

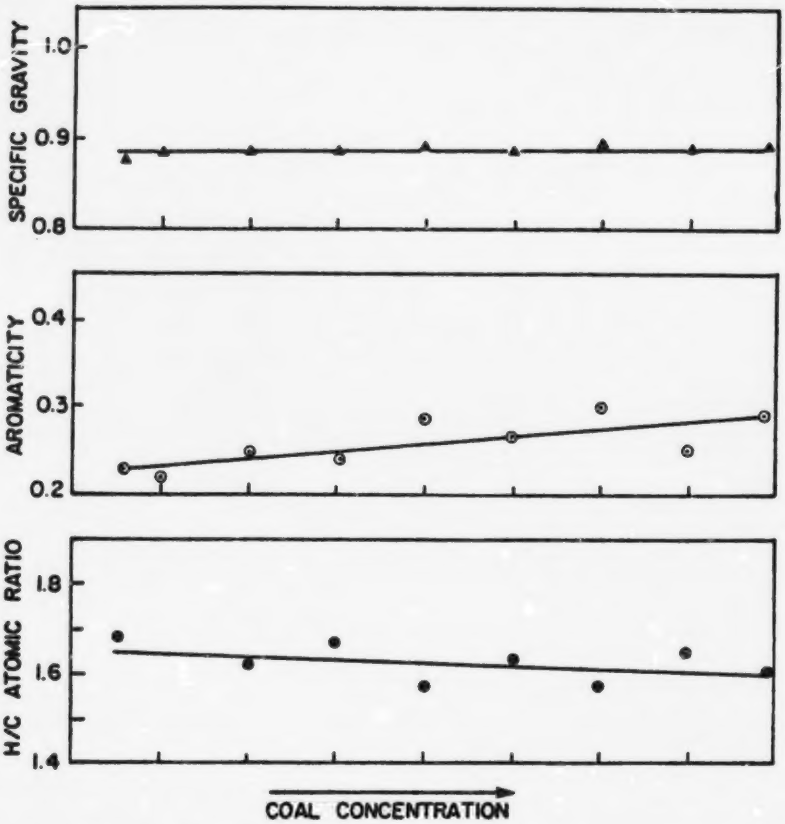

Fig. 19 – Distillate characteristics as a function of coal concentration

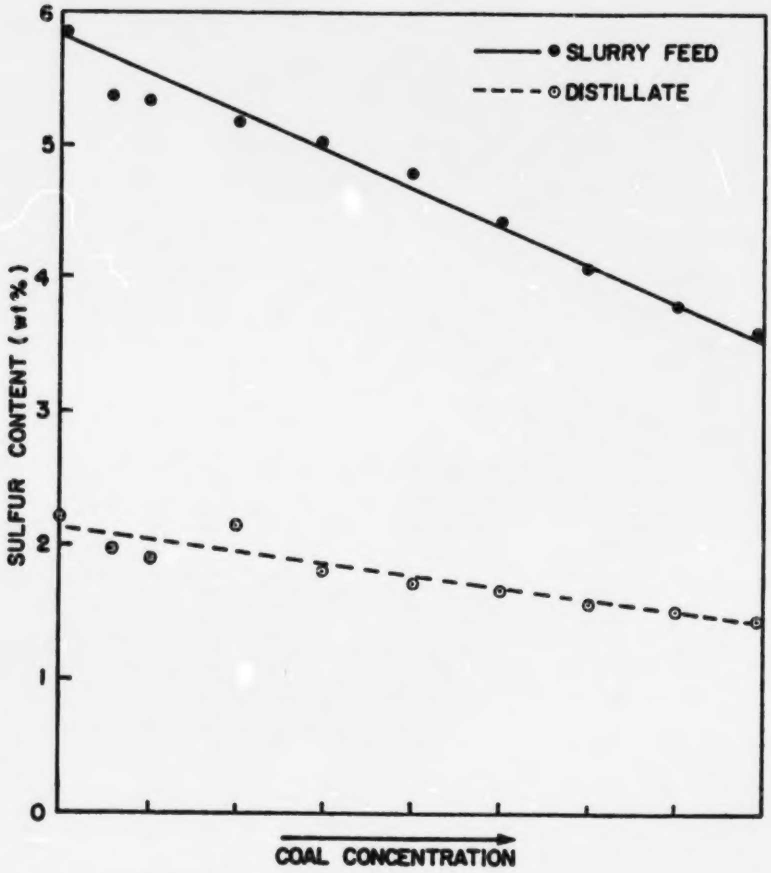

Fig. 20 – Sulphur content vs coal concentration

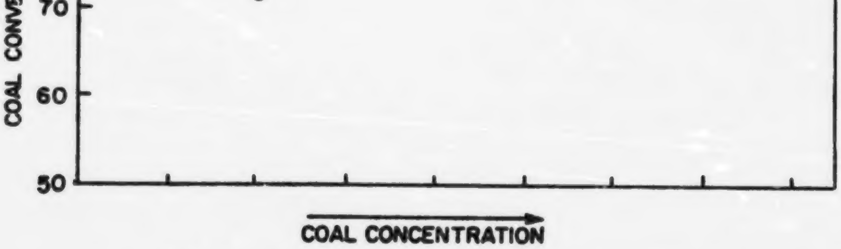

Fig. 21 – Coal conversion vs coal concentration

SESSION V: PAPER 22

COPROCESSING OF PETROLEUM RESIDUES AND COAL

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ABSTRACT

By coprocessing petroleum residues with coal at mild thermal conditions, the petroleum residues were upgraded and the coal was partially liquefied to yield valuable liquid and gaseous products. The upgrading of petroleum residues includes demetallation, production of distillates and viscosity reduction. The product could be used as a heavy fuel or hydrotreating and cracking feed.

This demetallation involves thermal breakdown of asphaltenic and metal-containing compounds in the residue, thermal breakdown of the coal with the formation of reactive radicals. These radicals then react with the metal-containing and carbonaceous fragments of the residue to form insoluble products on the unconverted coal which is conveniently removed.

Coal reactivity towards demetallation depends on coal rank with bituminous > subbituminous > lignite. Notwithstanding the great difference in the initial metals content, residues were demetallated to a comparable degree at similar conditions. Thus, this approach to demetallation is especially useful for high metals-containing petroleum-derived residues, heavy crudes, and tar sand bitumens.

**denotes speaker*

PRÉSENTATION 22

LE COTRAITEMENT DES RÉSIDUS DE PÉTROLE ET DE CHARBON

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RÉSUMÉ

Par le cotraitement des résidus de pétrole et du charbon, dans des conditions thermiques douces, les résidus de pétrole ont été valorisés et le charbon a été partiellement liquéfié pour obtenir des produits liquides et gazeux de valeur. La valorisation des résidus de pétrole comprend la démétallisation, la production de distillats et la réduction de la viscosité. Le produit pourrait être utilisé comme combustible lourd ou encore comme charge d'alimentation destinée à l'hydrotraitement ou au craquage.

La démétallisation comprend la décomposition thermique des composés asphalténiques et métalliques des résidus et la décomposition thermique du charbon avec la formation de radicaux réactifs. Ces radicaux réagissent ensuite avec les fragments carbonés et métalliques des résidus pour former des produits insolubles sur le charbon non converti, qui est ensuite facilement récupéré.

La réactivité du charbon à la démétallisation dépend du rang du charbon, selon qu'il s'agit de charbon bitumineux > sub-bitumineux > et de lignite. Nonobstant la grande différence dans la teneur métallique initiale, les résidus ont été démétallisés à un niveau comparable, dans des conditions semblables. Ainsi, cette façon d'aborder la démétallisation s'avère particulièrement utile dans le cas des résidus tirés du pétrole renfermant beaucoup de métaux, des bruts lourds et des bitumes tirés des sables bitumineux.

**indique le conférencier*

COPROCESSING OF PETROLEUM RESIDUES AND COAL

INTRODUCTION

In refineries crude oil is first distilled into fractions according to their boiling point. The fractions either become products or are used as feedstocks for subsequent processes. Material that is not distilled could either be an atmospheric tower bottoms or a vacuum tower bottoms, and is usually named long residue or short residue, respectively. The yields of such residues depend on the nature of the crudes and generally increase as a crude becomes heavier, i.e., as the API gravity of the crude decreases. Typical yields of 1000°F + bottoms can vary between 10 and 40% volume of the crude. However, some heavy oils such as Athabasca have residue yields in excess of 60%.

Low-cost refining of residues into more valuable products has been the objective of petroleum refiners and researchers. The development of and prospects for heavy oil upgrading technology have been reviewed recently (1).

Currently, the demand for heavy fuel, which is one of the major products from residues, is diminishing. The need to convert residues to gasoline and distillates is more pressing than ever.

The liquefaction of coal in petroleum residue has been the subject of several studies. Sakaki and coworkers have shown that coal may be solubilized by petroleum residue upon treatment for long periods of time at about 730°F (2). Similarly, others have observed that coal could be solubilized upon heating with hydrogenated vacuum residues or pitch for long periods of time at 600-770°F (3,4). The same group of workers has studied coal solvolysis by petroleum residues and has found that as reaction temperature increased, coal solubilization also increased, with the maximum for bituminous coal at about 73% (5). In all these studies, the potential of upgrading petroleum residues during the coprocessing of coal has not been examined.

In this paper we describe a novel approach to the utilization of residues in conjunction with coal, by which the residue is demetallated and thermally cracked, and the coal is liquefied.

EXPERIMENTAL

Materials

Two residues and a heavy crude with different metal contents were used in this study. The residues were commercially obtained refinery vacuum tower bottoms. The properties are shown in Table 1A.

Bituminous coal, subbituminous coal and lignite were used to study the effect of coal rank on residues-coal coprocessing. The properties are shown in Table 1B. For the adsorption study, silica gel with a 700 sq m/gm surface area was used.

Apparatus

The continuous flow reactor unit used in these experiments was a ⅜" OD x 1 ft stainless steel tube equipped with a means of feeding, heating, pressure control, product recovery and gas sampling.

Procedure

A typical experimental procedure was as follows. Upon pressurizing the unit to the required pressure with nitrogen, the furnace was switched on and the reactor was allowed to reach the required temperature. The feed pump was started for a line-out period of about 30 minutes. After the reactor system reached a steady state, the product was collected in a pressurized vessel until the required amount of feed was processed.

At the end of the run, the system pressure was reduced to atmospheric, and the product receiver was removed from the system. The product receiver was heated to 70°C to drain the product from the bottom of the receiver. Toluene was then added to the receiver to remove soluble material. This mixture was then drained and fresh toluene was added to the receiver until it was washed clean. Drained material and toluene washes were combined and the mixture was filtered through #42 paper on a Buchner funnel. The solid product on the filter paper was washed with additional toluene until it was no longer tacky. In small-scale experiments, the solid product was washed with toluene until the filtrate became clear. In large-scale runs, the solid products were extracted with toluene in a Soxhlet. Clean solid product was dried in a vacuum oven at 110°C to obtain the yield of solid for calculating the degree of coal conversion. The filtrate wash solution was combined and stripped at 70°C in the Rotavap to remove the solvent to obtain the liquid yield.

RESULTS AND DISCUSSION

In preliminary experiments, it was established that at about 850°F and a 12 liquid hourly space velocity (LHSV), the vacuum residue chosen was thermally cracked without the formation of toluene insolubles. Also, at the same operational conditions of temperature, pressure and LHSV in the presence of up to 30% added pulverized Illinois No. 6 coal, no plugging of the reactor took place. This is an important constraint on the process, as it would be uneconomical to run for short periods of time in commercial application.

Effect of Coal on Visbreaking

Yields of Products

Tables 2 and 3 show the yields and properties of the products obtained from thermal cracking of vacuum residue A alone and in admixture with varying amounts of pulverized Illinois No. 6 coal at 850°F, 400 psig and 12 LHSV.

In determining liquid recovery for these experiments, toluene was used to dissolve the non-solid component of the mixtures. Under the process conditions used, it was shown that no solid is formed when vacuum residue is processed alone. The solid product is considered to be unconverted coal and entirely contributed by coal. The yield data reported for residue coprocessed with coal is based on the amounts of gas measured, the known initial composition of the residue/coal mixture and the amount of liquid and solid products physically recovered after coprocessing.

In mild thermal cracking of vacuum residues, only small amounts of gas are usually produced. However, when coal was coprocessed under the same process conditions the amount of gas produced increased. Also, as the amount of added coal was increased, the amount of gas generated also increased. These results indicate that coal liquefaction contributes to the formation of these additional gases. The fraction of coal conversion to gas decreases from 37 to 12% as the coal addition was increased from 5 to 30%, and the coal conversion decreased from 78 to 46%.

Since no solid was formed upon thermal cracking the residue alone, all the solid recovered after processing is assumed to be composed of unconverted coal that was added. In the presence of coal, the carbonaceous fragments from the residue could contribute to the solid yield slightly, but it was neglected in the calculation. The unconverted coal is calculated as a percentage of the added coal from which the total conversion of coal is derived by difference. The coal conversion decreased from 78 to 46% as the percentage of coal addition was increased from 5 to 30%. This 40% decrease in coal conversion is expected since the overall increase in added coal was 600%.

Coal solubilization was determined by subtracting the contribution of the residue to the total liquid product recovered. For example, for 100 grams of 10/90 coal/residue mixture, the total liquid recovered was 92.5% of the mixture. Now the residue alone produces 89.1 gms of liquid, i.e., 99% of 90. However, the actual yield was 92.5 gms, i.e., a 3.4 gm increase in the liquid yield. We believe that this 3.4 gms increment came from the 10 gm of coal which is 34% of the added coal, as shown in Table 2. For the other amounts of added coal, the solubilization percentages were 41, 37 and 34 for 5, 20 and 30% added coal, respectively. These results are consistent with those of Osafune et al. who reported 48% solubilization, for a 1:2 coal residue mixture. However, they used another bituminous coal and Khafji asphalt coprocessed at about the same temperature (5).

Product Quality

Gas produced during thermal cracking of a petroleum-derived residue contains low molecular weight hydrocarbons such as methane and ethane with trace amounts of other gases. When coal was added to the feed, however, the gaseous product contained significant amounts of carbon monoxide and carbon dioxide as the result of coal devolatilization. This is further support that coal liquefaction in the resid-coal coprocessing contributes to production of additional gaseous product.

It is well known that visbreaking alone does not reduce the metals content of a residue. This is confirmed by the data for residue alone (Table 2). The addition of coal to the feed before cracking, however, reduced the metals content of the cracked product, and the effect increases with coal concentration up to a maximum at 30% coal (Fig. 1). The metals removed from the residue appear in the solid recovered. For example, for the 20% added coal experiment, whereas the initial Ni/V concentrations in the added coal were 65/20, the final concentrations in the recovered solid were 130/535 ppm. Similarly for the other experiments, the recovered solid contained a higher concentration of Ni/V than the coal. Notwithstanding the crudeness of the experimental procedures, reasonably good metals balance could be made for all of the runs carried out.

The other property determined for the liquid product was Conradson Carbon Residue (CCR). In this case no significant change was observed. This suggests that the additional liquid generated from the coal does not have a significant propensity for coke formation. In fact, for the 30% added coal case a reduction of 1% in the CCR content of the liquid product is observed. Of course, we cannot rule out the possibility that some of the CCR from the residues was removed as a deposit on the unconverted coal.

At the operating conditions of 850°F, 400 psig and 12 LHSV tested, the extent of residue demetallation increased as the amount of added coal was increased. The removal of Ni increased from 7% to 40% as the coal was increased from 5% to 30% (Fig. 1). The Ni removal appears to peak at 40% at this temperature. The V removal showed a similar trend to that of Ni.

As the temperature of coprocessing was increased from 850 to 870°F, the extent of demetallization of the residue also increased (Table 4). This is shown by the concentration of metals in the recovered liquid which was lower than that obtained by coprocessing at 850°F, for both 20% and 30% added coal (Tables 3 and 4). Thus by increasing the severity of cracking, further demetallation is achieved. For example, for 30% added coal, the demetallation is 40% vs 53% for nickel and 46% vs 73% for vanadium at 850 and 870°F, respectively.

The metals that remain in the liquid product can be reduced further by additional processing steps. This could be carried out using a treating step that would remove components with which metals are usually associated. A demonstration of this possibility was the use of n-heptane as a high molecular weight deasphalting solvent. As shown in Table 5, whereas the 17% heptane insolubles (asphaltenes) contain 120/470 ppm Ni/V, the 83% soluble product (maltenes) had only 10/32 ppm Ni/V. These Ni/V residue concentrations correspond to 81% and 89% demetallation, respectively.

Coal solubilization during coprocessing is suggested by the elemental oxygen content of the product. Coal is known to contain more oxygen than crude oils or their residues. Thus, a change in the oxygen content would be a reasonable indication of the contribution of the coal to the liquid product. The heavy distillate or the maltenes produced from crude oil by solvent deasphalting contain little or no oxygen. Heptane deasphalted oil from Residue A used in this study contains 0.2% oxygen and the asphaltenes isolated contain 1.0% oxygen. Thus by comparing this *normal* oxygen content with that of the product obtained by coprocessing with coal, we should be able to determine if the coal was solubilized.

It was observed that both the maltenes and the asphaltenes from the products of residue/coal coprocessing showed a significant increase in oxygen content, confirming coal solubilization as a source of the extra liquid product. The observed oxygen values were 0.2% vs 0.76% for the maltenes and 1% vs 2.66% for the asphaltenes. These data are outside the limits of analytical accuracy and are in agreement with data published by others (6).

Demetallation and Coal Rank

The results obtained so far show that in coprocessing, bituminous coal plays several roles. The coal removes metals from a petroleum residue, contributes to the gas and the liquid yields, and is the sole source of solid product. Thus it was of interest to determine if coals of different rank would behave in a similar manner.

The results of coprocessing bituminous and subbituminous coal and lignite with vacuum residue A at 870°F, 400 psig and 12 LHSV are shown in Table 5. The three types of coal used showed different reactivity towards the residue and liquefaction. As would be predicted the subbituminous coal and lignite, which have a lower volatiles content than the bituminous coal, also show lower solubilization than the bituminous coal. At 20% of coal addition, the coal conversions were 46, 30 and 33% for bituminous, subbituminous and lignite, respectively.

The three different rank coals also showed significant differences in the effectiveness of metal removal (Table 6). Effectiveness decreased in the order:

Bituminous > Subbituminous > Lignite

For example, the vanadium removals were 73 and 27% for the bituminous coal and lignite, respectively.

Adsorption of large organic molecules on charcoal, alumina, nodules and other solids is a well-known phenomenon. It was thus considered essential to determine if this observed demetallation of the residue is adsorptive in nature. Two approaches were used. In the first, vacuum residue was coprocessed in admixture with chemically non-reactive Davidson's Grade 12 Silica Gel, 700 sq m surface area/gm, at 870°F, 400 psig and 12 LHSV. Notwithstanding the high surface area of the silica gel, the Ni and V removals were only 9 and 13%, respectively (Table 7). These levels were much lower than the 47 and 52% obtained for the bituminous coal. In the second approach, the residue in toluene solution was allowed to contact pulverized bituminous coal for 72 hours at room temperature. The bituminous coal at room temperature is obviously non-reactive because the degrees of Ni and V demetallation were merely 2 and 1% respectively. These observations suggest that physical adsorption makes a very small contribution to the total demetallation observed with bituminous coal. The results from coprocessing with silica gel would suggest that the physical adsorption should lead to less than 9 and 13% of Ni and V removals, respectively. Furthermore, the fact that demetallation increases as the operation temperature and severity is increased suggests that the demetallation reaction is a chemically activated process, and not a simple physical adsorption of large metal-containing organic species on the coal residue.

Based on the results, we believe that the demetallation of residues involves the following steps:

1. Thermal break-down of metal-containing and asphaltenic compounds in the residues.
2. Thermal conversion and liquefaction of coal leading to reactive radical species.
3. Conversion of metal and carbonaceous fragments from residues to solids by reaction with the radicals from the coal. The radicals from the dissolved coal serve as the metal scavengers, while the unconverted coal serves as the carrier to deposit insoluble metal reaction products which can be readily separated from the liquid product.

Demetallation and Petroleum Source

For the three petroleum substrates used in this study, vacuum residue A, vacuum residue B and Boscan crude, slurried with 30% Illinois No. 6 coal, the extent of vanadium removal at 870°F and 12 LHSV is 73%, 57% and 51% (Table 8), respectively. The susceptibility of the three materials for nickel removal in terms of % demetallation does not vary significantly. However, the actual *amount* of metal removed increased as the initial metal content of the substrate increased. For example, 620 ppm of Vanadium was removed from Boscan crude, i.e., 51% demetallation and 106 ppm of Vanadium was removed from Residue B, i.e., 57% demetallation. Thus, this approach to demetallation is most useful for high metals containing petroleum-derived residues or heavy crudes or tar sand bitumens.

These observations indicate that demetallation of residues is not limited by the initial amount of metal present in the residue and could be related to the types of structures with which the metals are associated. It appears, however, that in this demetallation process, about 50% of the metals are reactive toward coal and are easily removed by coprocessing. The remaining 50% are less reactive and may require processing of a different nature. Our observations are consistent with those reported by Sugihara who has found that there are two types of metal-containing species in petroleum (7).

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TABLES

Table 1A – Properties of residues and Boscan crude

	Residue A	Residue B	Boscan crude
Gravity, °API, 60/60°F	6.1	4.8	10.1
Conradson carbon residue (CCR) % wt	19	23	16
Asphaltenes, % wt	9.2	—	—
Viscosity, cS at			
130°F	271 715	—	—
212°F	2 342	12 000	3 786
Nickel, ppm	53	58	106
Vanadium, ppm	250	186	1 220
Ash, % wt	0.1	0.1	0.1

Table 1B – Properties of coals

	Bituminous	Subbituminous	Lignite
Elemental analyses			
Carbon, % wt	80.9	65.5	54.4
Hydrogen, % wt	5.3	5.7	5.4
Nitrogen, % wt	1.6	0.9	0.7
Sulphur, % wt	1.3	0.2	0.5
Oxygen, % wt	7.8	15.6	32.0
Ash, % wt	2.8	4.0	5.8

Table 2 – Conversion of residue A and coal in coprocessing (850°F, 400 psig, 12 LHSV)

	Coal: Illinois #6 Residue: A				
Coal, % wt	0	5	10	20	30
Residue, % wt	100	95	90	80	70
Yield, % wt					
Gas	1	2.8	3.4	3.9	4.3
Liquid	99	96.1	92.5	86.6	79.5
Solid	0	1.1	4.1	9.5	16.2
Total coal conversion, %	—	78	59	53	46
% of coal solubilized	—	41	34	37	34
% of coal converted to gas	—	37	25	16	12

Table 3 – Coprocessing of vacuum residue A and its mixtures with Illinois #6 coal (850°F, 400 psig, 12 LHSV)

Coal, % wt	0	5	10	20	30	100
Residue A, % wt	100	95	90	80	70	0
Properties						
Gravity, °API, 60/60°F	6.1	—	—	—	—	—
Conradson Carbon residue (CCR), % wt	19	—	—	—	—	—
Asphaltenes, % wt	9.2	—	—	—	—	—
Viscosity, cS at,						
130°F	271 715	—	—	—	—	—
212°F	2 342	—	—	—	—	—
Nickel, ppm*	53	54	54	55	57	65
Vanadium, ppm*	250	238	227	205	181	20
Ash, % wt	0.1	—	—	—	—	10
Liquid product						
Gravity, °API, 60/60°F	5.7	5.7	5.7	6.2	7.6	—
Asphaltenes, % wt	15.2	—	—	—	—	—
CCR, % wt	19	—	19	19	18	—
Viscosity, cS at						
130°F	622	—	—	—	—	—
212°F	112	—	—	—	—	—
Nickel, ppm	53	50	42	34	32	—
Vanadium, ppm	243	216	181	146	131	—
Solid product						
Nickel, ppm	—	195	135	130	80	65
Vanadium, ppm	—	905	495	535	225	20

** Calculated for the mixtures*

Table 4 – Demetallation of residue A by added Illinois #6 coal upon coprocessing (870°F, 400 psig, 12 LHSV)

Coal, % wt	20	30
Residue, % wt	80	70
Liquid product		
Gravity, °API	5.7	5.7
Asphaltenes, % wt	—	17
CCR, % wt	19	19
Nickel, ppm (%)*	29 (45)	25 (53)
Vanadium, ppm	120 (52)	67 (73)
Solid product		
Nickel, ppm	—	110
Vanadium, ppm	—	360

** Data in parentheses represent extent of demetallation of processed residue*

Table 5 – Heptane deasphalted liquid product obtained from coprocessing vacuum residue A with 30% Illinois #6 coal (870°F, 400 psig, 12 LHSV)

	Heptane solubles	Heptane insolubles
% wt to liquid product	83	17
Nickel, ppm	10	120
Vanadium, ppm	32	470
Elemental analysis, % wt		
C	84.68	84.67
H	10.63	6.10
N	0.39	1.32
S	3.45	5.19
O	0.76	2.66

Table 6 – Demetallation of vacuum residue A with coals of different volatilities at 870°F, 400 psig 12 LHSV

Coal	Bituminous*		Subbituminous		Lignite
% coal added	20	30	20	30	30
% residue	80	70	80	70	70
Yield, % wt					
Gas	—	—	5	4	4
Liquid	—	—	82	75	76
Solid	—	—	13	21	20
% of coal converted	53	46	35	30	33
% of coal solubilized	37	34	10	17	20
% Demetallation					
Nickel	45	53	32	38	23
Vanadium	52	73	31	36	27
Liquid product					
Nickel, ppm	29	25	36	33	41
Vanadium, ppm	120	67	173	160	182

* *Conversion and solubilization data for 850°F*

Table 7 – Coprocessing of vacuum residue A in admixture with silica gel (grade 12) and attempted adsorption of metals on coal from a toluene solution of vacuum residue

	Silica gel*	Bituminous coal**
% solid, % wt	20	30
% residue, % wt	80	70
Demetallation, %		
Nickel	9	2
Vanadium	13	1
Liquid properties		
Nickel, ppm	48	52
Vanadium, ppm	218	248

* *At 870°F, 400 psig, 12 LHSV; surface area 700 sq m/gm*

** *At toluene at room temperature*

Table 8 – Demetallation of three petroleum components by coprocessing with Illinois No. 6 coal at 870°F, 400 psig and 12 LHSV

Crude	Vac. residue A*			Vac. residue B			Boscan		
% coal added	0	20	30	0	20	30	0	20	30
% petroleum component	100	80	70	100	80	70	100	80	70
Yield, % wt									
Gas	1	3.9	4.3	—	—	—	—	—	—
Liquid	99	86.6	79.5	—	—	—	—	—	—
Solid	—	9.5	16.2	—	—	—	—	—	—
% of coal conversion	—	53	46	—	25	—	—	—	—
% of coal solubilized	—	37	34	—	—	—	—	—	—
% demetallation									
Nickel	—	45	53	—	36	55	—	43	45
Vanadium	—	52	73	—	44	57	—	46	51
Liquid product									
Nickel, ppm	53	29	25	58	37	26	106	60	58
Vanadium, ppm	250	120	67	186	105	80	1220	656	600
Solid product									
Nickel, ppm	—	—	110	—	160	110	—	155	210
Vanadium, ppm	—	—	360	—	225	250	—	1880	1690

* *Yield conversion and solubilization data for 850°F*

FIGURE

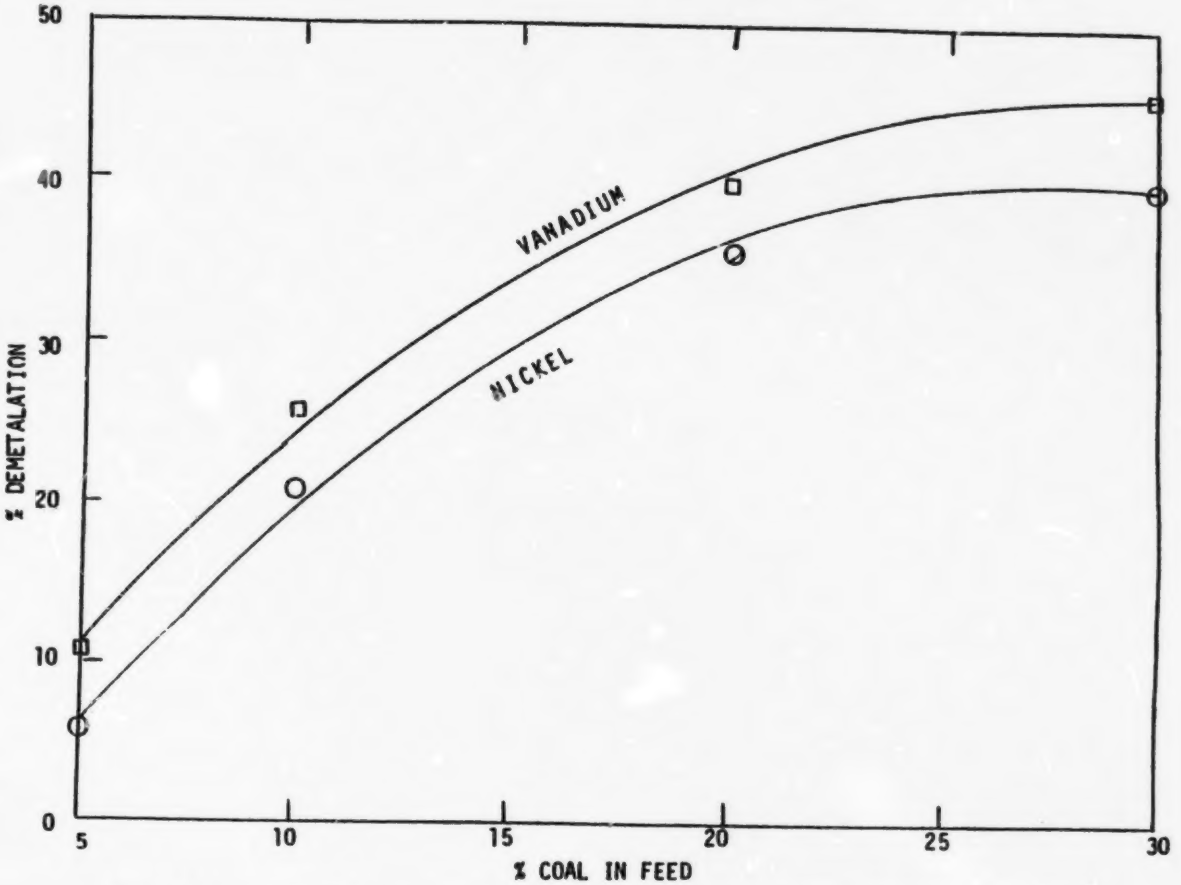

Fig. 1 – Demetallation of vacuum residue A by Illinois No. 6 coal at 850°F, 400 psig and 12 LHSV

SESSION I: PAPER 23

COPROCESSING COAL AND PETROLEUM RESID

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ABSTRACT

The integration of coal liquefaction and petroleum resid upgrading has been a natural extension of the Signal UOP expertise in each individual area. Initial work was conducted in laboratory batch experiments processing coal and petroleum resid with hydrogen in the absence of added catalyst. It was found that petroleum resids were excellent solvents for coal liquefaction with coal conversions running between 80 to 90%. Coprocessing also resulted in 44 to 93% demetallization of the resid. A subsequent development involved the utilization of catalysts. This methodology gave significant improvement, resulting in increased coal conversion and reduced metals and asphaltenes in the liquid product. Processing with catalyst resulted in 90 to 93% conversion of coal, 97 to 99% demetallization, and 75 to 86% reduction in asphaltenes. The liquid hydrocarbon recovered from the process constitutes a high quality, synthetic oil which can be utilized as a feedstock in existing petroleum refineries.

**denotes speaker*

PRÉSENTATION 23

LE COTRAITEMENT DU CHARBON ET DES RÉSIDUS DE PÉTROLE

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RÉSUMÉ

L'intégration de la liquéfaction du charbon et de la valorisation des résidus de pétrole s'est avérée un prolongement naturel de l'expertise de Signal UOP, dans chaque secteur individuel. Le travail initial a été fait lors d'expériences en laboratoire où l'on a traité des lots de charbon et des résidus de pétrole avec de l'hydrogène, sans catalyseur ajouté. On a constaté que les résidus de pétrole constituaient d'excellents solvants pour liquéfier le charbon et que les conversions du charbon s'établissaient entre 80 et 90 %. Le cotraitement s'est également traduit par une démétallisation des résidus variant entre 44 et 93 %. Dans un développement ultérieur, on a utilisé des catalyseurs. Cette initiative a produit des améliorations marquées, qui seront traduites par une conversion accrue du charbon et une réduction des métaux et des asphaltènes dans le produit liquide. Le traitement avec un catalyseur s'est traduit par une conversion du charbon de 90 à 93 %, une démétallisation s'établissant entre 97 et 99 % et une réduction des asphaltènes variant entre 75 et 86 %. Les hydrocarbures liquides récupérés grâce à ce procédé constituent un pétrole synthétique de grande qualité qui peut servir de charge d'alimentation dans les raffineries de pétrole existantes.

**indique le conférencier*

COPROCESSING COAL AND PETROLEUM RESID

INTRODUCTION

Industrial nations around the world are focusing attention on the production of transportation fuels from alternative energy sources. Coal and petroleum resid are two abundant resources that can be converted to transportation fuels. The conversion of these materials into high quality products is difficult and expensive. Improved technology is needed to convert these materials efficiently and economically.

With a background of research activities in both coal conversion and petroleum resid upgrading, researchers at Signal UOP, in 1970, conceived a new processing concept with integrated coal liquefaction and petroleum resid upgrading. Premium synthetic liquids are produced by the simultaneous liquefaction of coal and upgrading of petroleum resid. This paper reviews laboratory results and subsequent development of the coprocessing concept.

SIGNAL UOP'S BACKGROUND IN RESID CONVERSION

The Signal UOP Research Center has a broad range of experience in the resid processing area with an aggressive research and development program. The involvement in this processing area contains the same elements that have made UOP a successful company since 1914: basic research, process development and commercialization. Examples of resid processes developed by UOP are the world's first atmospheric resid desulphurizer (RCD Unibon®), which began operation in 1967, and the first successful vacuum bottoms hydrocracker, which came on stream in 1972 [RCD Unibon (BOC)].

UOP has developed resid conversion processes that include examples in each of the major types of processes (1):

Process category	*Process name*
Separation	Vacuum fractionation Demex® (Solvent deasphalting)
Thermal	Visbreaking Thermal cracking Coking
Catalytic	RCD Unibon RCD Unibon (BOC) RCC^{SM} Aurabon®

SIGNAL UOP'S COAL-PROCESSING BACKGROUND

The Research Center entered into coal research prior to the 1973 energy crisis when it became evident in the mid-1960's that finding oil was becoming more difficult and costly. The principal research objectives in this field involved developing conversion processes for producing:

- The maximum yield of premium fuel
- Coal liquids that are free of ash and solids
- Coal liquids that are processible in conventional refining equipment.

The early research program was carried out as batch experiments in autoclaves and advanced through research-scale pilot-plant programs, culminating in 1974 with the development of UOP's two-stage coal liquefaction process. A schematic flow diagram of this process is shown in Figure 1. Key features include:

- The use of a full boiling range coal-derived solvent with enhanced hydrogen donor potential
- The capability of effective liquid-solid separation
- The integrating of a second-stage, fixed-bed catalyst.

Early in this research effort, it was recognized that two-stage coal liquefaction processes are capital intensive. In an effort to reduce the complexity and cost of the process, a single-stage catalytic coal liquefaction process was developed. A schematic flow diagram of this process is shown in Figure 2. A key feature is incorporation of the hydrotreating function in the first stage. Integration of liquefaction and hydrotreatment produced liquid yield and product quality comparable, or better than, that obtained in the two-stage coal liquefaction process.

COPROCESSING COAL AND PETROLEUM RESID

The integration of coal liquefaction and petroleum resid upgrading was a natural extension of the Signal UOP expertise in each individual area and evolved from the need to reduce the cost of coal liquefaction processes, while also maximizing the yield of premium liquid product. Inherent in coal liquefaction processes is the need to recycle large amounts of solvent. Reducing or eliminating the recycle and reconditioning of the solvent should improve the economics. Using petroleum resids as solvents offered the possibility of a once-through process, eliminating the need for solvent recycle and producing a maximum amount of premium liquid product. Development of the coal/resid coprocessing concept began in 1970.

Signal UOP has continued work in the coprocessing area and has developed catalytic coprocessing, the use of catalyst to catalyze the conversion of coal and upgrading of petroleum, as a further improvement of the original concept. A schematic flow diagram of this process is shown in Figure 3. Key features are:

1. The properties and preparation of the coal liquefaction solvent are de-coupled from the coal.
2. The simplicity of a single-stage once-through process will reduce capital and operating costs.
3. Simultaneous conversion and upgrading converts the coal and petroleum resid into lighter synthetic oil of higher value.
4. An active catalyst effectively stabilizes the initial products from coal depolymerization and resid conversion reactions.
5. The liquid hydrocarbon produced constitutes a high quality synthetic oil which can be utilized as a feedstock in existing refineries.

Signal UOP has conducted several experimental programs to further develop the coprocessing concept. The initial work was carried out in laboratory batch experiments processing coal and petroleum resid with hydrogen in the absence of catalyst. The coal used in this work was Illinois No. 6. A typical analysis is shown in Table 1. Among the petroleum types evaluated in our program were Light South Louisiana, San Ardo (Heavy Californian), tar sand bitumen (Canadian), and Boscan (Heavy Venezuelan). Key properties of these materials are shown in Table 2. The tests were conducted in a 1800-mL rocking autoclave.

The key results of these non-catalytic experiments are summarized in Table 3. Petroleum resids were found to be good solvents for coal liquefaction. Coal conversions ranged from 80 to 90%. The heavier resids, topped Boscan, tar sand bitumen, and San Ardo were more effective solvents (88-90% conversion) than the Light South Louisiana (80%). Coprocessing also resulted in 44 to 93% demetallization of the resid. The reduction of metals is most dramatic for topped Boscan, the most metal-contaminated feedstock, with approximately 93% of the metals being removed in the process.

Other coprocessing experimental programs were conducted using catalyst to catalyze the conversion of coal and upgrading of the petroleum resid. Catalyst systems using molybdenum were investigated. These tests were conducted under the same conditions as the non-catalytic experiments, with catalyst concentrations equal to 8 wt % of the coal feed, or approximately 2.7 wt % of the total charge to the autoclave.

The key results of these catalytic experiments are summarized in Table 4. These results demonstrate the attractive features and advantages of the catalytic coprocessing concept. Compared to the cases with no catalyst, the experiments with catalyst showed:

- increased coal conversion
- reduced liquid product metals
- reduced liquid product asphaltenes.

Coprocessing with catalyst resulted in 90 to 93% conversion of the coal, 97 to 99% demetallization, and 75 to 86% reduction in asphaltenes. The reduction in metals and asphaltenes was most dramatic for the heavily contaminated feedstocks. The topped Boscan had a 79% reduction in asphaltenes and a 99% reduction in metals. The tar sand bitumens showed an asphaltene reduction of 86% and a reduction in metals of 99%.

The distribution of product from the autoclave catalytic coprocessing studies of the tar sand bitumen is shown in Table 5. A liquid yield in excess of 90 wt % was achieved with substantial amounts of the liquid product being in the distillate and gas oil boiling ranges. Light hydrocarbon gas products were low while consumption of hydrogen was 3.8 wt %. High liquid and low gas yields indicated good utilization of this hydrogen. The product distribution did not appear to be different from what would be obtained when processing coal or petroleum resid individually.

FURTHER DEVELOPMENT OF COPROCESSING CONCEPT

Past experimental work conducted in small scale has shown that it is possible to use coal and petroleum resid in a coprocessing concept. Further development work is needed before it can be determined if this coprocessing concept offers the potential for improved economics. Among the topics to be investigated further are:

- the properties of petroleum resid which are most important for coal conversion
- the effect of different coal types on coal conversion and resid upgrading
- the amount of catalyst required for efficient conversion of the coal/resid mixture
- the effect of coal conversion (reactor severity) on hydrogen consumption and product quality
- the complete description of the products and an accurate estimate of the processing operations needed to produce finished products
- the preferred combination of coal/resid conversion unit severity, overall conversion unit flow scheme, and integration with the refining operation.

The UOP Process Division was recently awarded a contract by the U.S. Department of Energy to evaluate coal liquefaction coprocessing. The overall objectives of this work are to evaluate the technical feasibility of coprocessing and to establish a process database on the coprocessing concept. Specific objectives will be to establish the overall criteria for selection of coal types and petroleum characteristics, to evaluate process performance, and to estimate the cost of a conceptual commercial facility. The experimental work for this program will be conducted by the Signal UOP Research Centre.

SUMMARY

The Signal UOP Research Center's background in resid and coal processing led to the coprocessing concept – the integration of coal conversion and petroleum resid upgrading. This concept has been investigated in laboratory batch experiments, where petroleum resids were found to be excellent solvents for coal liquefaction. Coal conversions as high as 90% were obtained, while significant reductions in the metals contents of the resids were also achieved. The reduction in metals was most dramatic for the more heavily contaminated feedstocks. The coprocessing concept was further improved by the use of catalyst to catalyze the conversion of coal and upgrading of the petroleum resid. This resulted in:

- increased coal conversion
- reduced liquid product metals
- reduced liquid product asphaltenes.

Active catalyst in conjunction with relatively low reaction temperatures allows high coal conversions to be achieved without cracking of coal and resid by-products to light gases. Because thermal degradation reactions are minimized, maximum yield of high quality liquid hydrocarbons is achieved. The combined effect of these advantages is lower hydrogen consumption and better overall hydrogen utilization. The liquid hydrocarbon recovered from the process represents a high quality synthetic oil which can be utilized as a feedstock in existing petroleum refineries.

Combining coal liquefaction with upgrading of petroleum resid currently offers the potential of being an improved approach for using coal and low quality petroleum resids to increase the amount of available oil for our energy needs.

REFERENCES

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TABLES

Table 1 – Typical analysis of Illinois No. 6 coal

Carbon	67.83 wt %
Hydrogen	5.14
Oxygen	9.45
Sulphur	3.01
Nitrogen	1.21
Ash	7.91
Moisture (H_2O)	1.64

Table 2 – Key properties of petroleum resids

Solvent	Light South Louisiana crude	San Ardo crude	Tar sand bitumen	Topped Boscan crude
API gravity @ 60°F	34.8	13.8	9.2	5.4
Hydrogen, wt %	12.80	11.28	10.12	10.6
Heptane insol., wt %	0.03	4.75	10.22	19.04
Metals, wt ppm	10	112	162	1630

Table 3 – Results of non-catalytic coprocessing experiments

	Light South Louisiana	San Ardo crude	Tar sand bitumen	Topped Boscan crude
Conversion of MAF coal, wt %	79.9	88.3	88.1	90.9
Yields				
Liquid product, wt %	70.1	83.5	83.2	89.7
Liquid product analysis				
H_2, wt %	12.40	10.72	9.08	9.70
C_7 insolubles, wt %	0.23	11.25	16.37	18.3
Total metals, wt ppm	1.8	29	73	115

Table 4 – Results of catalytic coprocessing experiments

	Light South Louisiana crude	Sano Ardo crude	Tar sand bitumen	Topped Boscan crude
Conversion of MAF coal, wt %	93.4	93.2	90.1	92.5
Yields				
Liquid product, wt %	76.1	80.4	79.5	86.4
Liquid product analysis				
H_2, wt %	11.81	11.60	10.12	10.70
C_7 insolubles, wt %	1.30	1.01	1.24	3.15
Total metals, wt ppm	<1	3	1.4	8.3

FIGURES

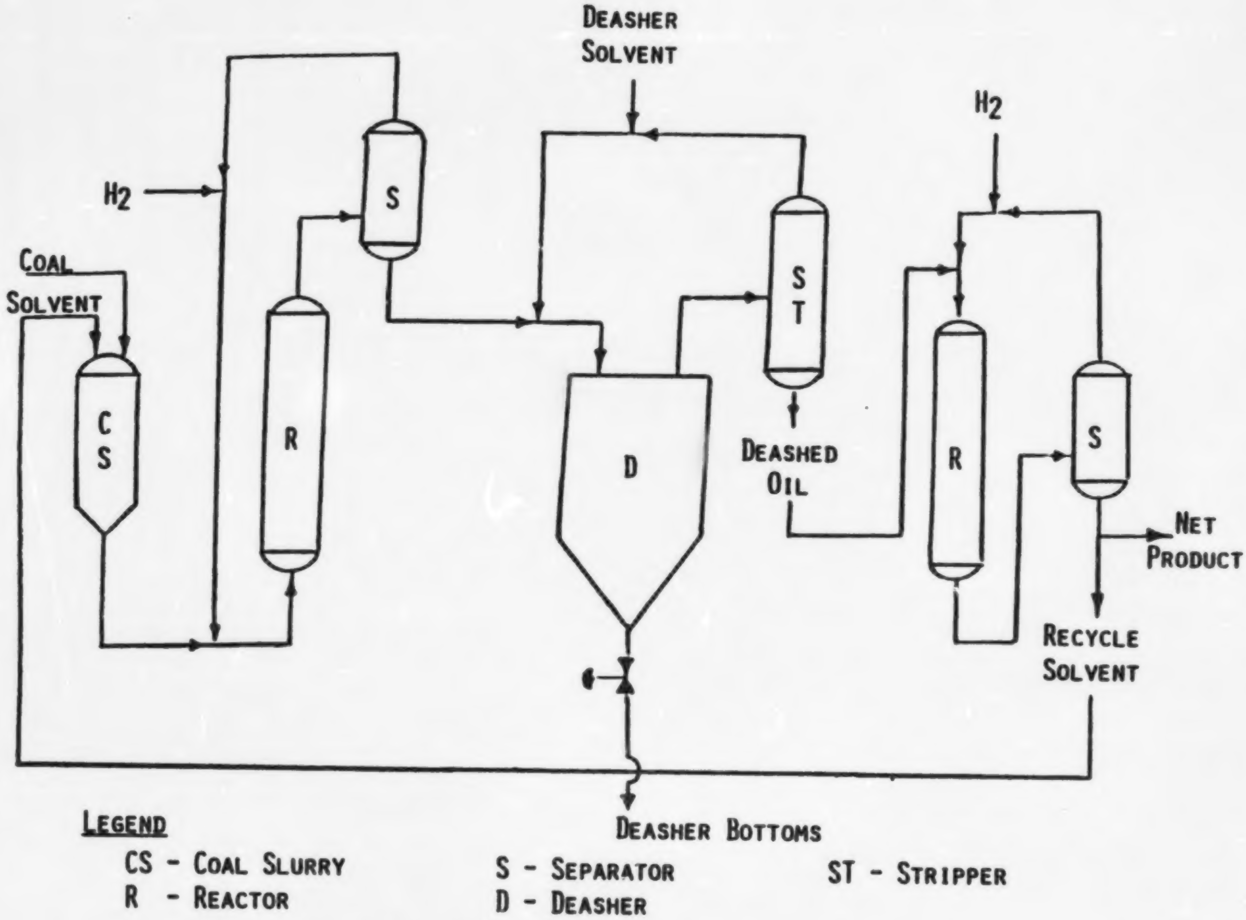
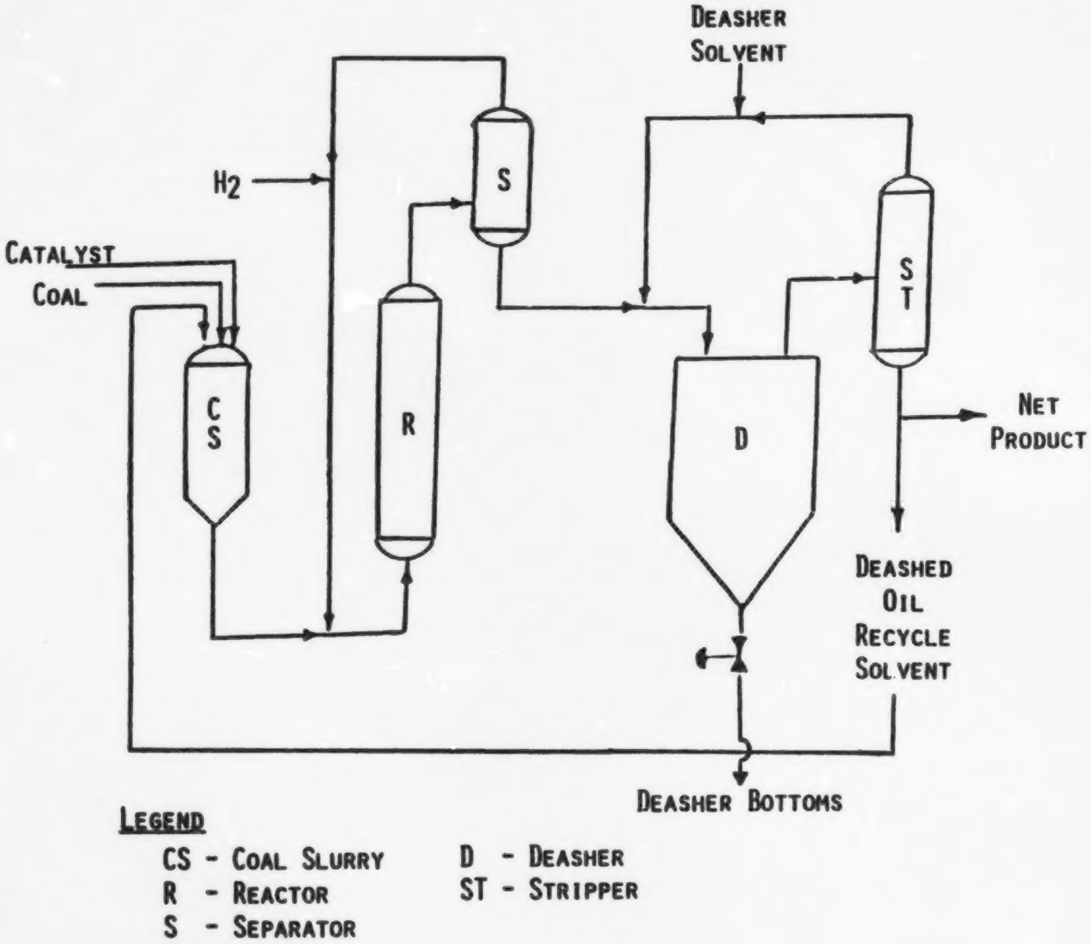

DEASHER SOLVENT
H2
H2
COAL
SOLVENT
S
C S
R
S T
D
DEASHED OIL
R
S
NET PRODUCT
RECYCLE SOLVENT
DEASHER BOTTOMS
LEGEND
CS - COAL SLURRY
R - REACTOR
S - SEPARATOR
D - DEASHER
ST - STRIPPER

Fig. 1 – UOP two-stage coal liquefaction – process flow diagram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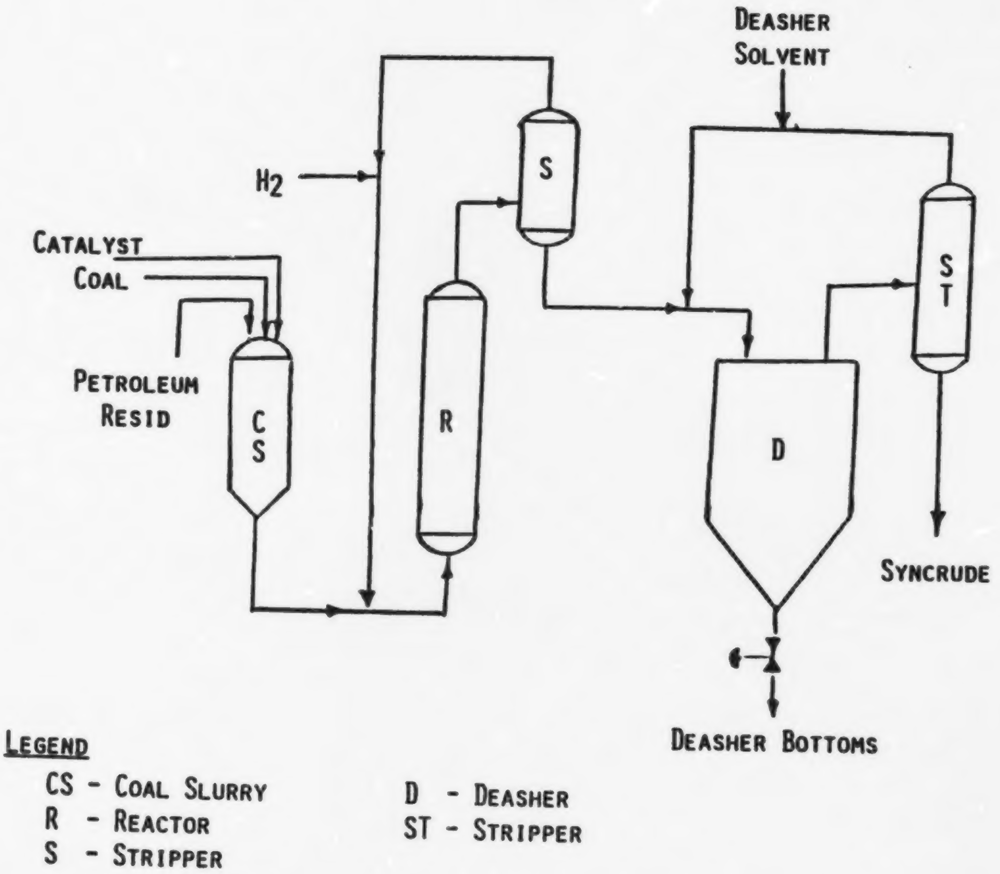
NET PRODUCT
DEASHED OIL RECYCLE SOLVENT
DEASHER BOTTOMS
LEGEND
CS - COAL SLURRY
R - REACTOR
S - SEPARATOR
D - DEASHER
ST - STRIPPER

Fig. 2 – UOP single-stage catalytic coal liquefaction – process flow diagram


DEASHER SOLVENT
H2
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CATALYST
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PETROLEUM RESID
CS
R
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D
SYNCRUDE
DEASHER BOTTOMS
LEGEND
CS - COAL SLURRY
R - REACTOR
S - STRIPPER
D - DEASHER
ST - STRIPPER

Fig. 3 – UOP catalytic coprocessing – process flow scheme

SESSION V

DISCUSSION

MODERATOR: J.M. DENIS, CANMET/ERL

DENIS (CANMET): In direct coal liquefaction the solvent is always a process-derived material and normally it is compatible with the feedstock. In coprocessing this marriage of solvent and coal is not always possible. So the question I would like to ask the panel is, do we really have to be concerned about marrying a coal and a resid feedstock to form a slurry?

GATSIS (UOP): I don't think you have to be, at least in my work to the present time, where I've only worked with one coal. In the DOE contract, we're going to use four coals and six petroleum resids. I'm sure we will see effects between different types of coals, in other words, bituminous, subbituminous and lignite coals. As far as the differences we'll see within bituminous coal, I think there will be some subtle differences.

YAN (MOBIL): First of all, many years ago we tried to start with just one coal, a bituminous coal, and different kinds of residue and petroleum refining streams to assess their effectiveness. Now, if you are really interested in coal conversion, the petroleum residue has a significant effect. For example, in a petroleum refinery, if you can use the aromatic stream which you get from the catalytic cracker bottoms, it is an excellent liquefaction solvent. In fact, it is as good as or better than the coal-derived materials. If we don't have that much of this material we have to take what residue we have. People are always worried about the compatibility that this morning's speakers were talking about and, yes, compatibility is very important.

Compatibility can become very serious when your residue hydrocarbon oil is very light. However, we normally cannot afford to have a light oil to use as a solvent and you always have to go to a heavy residue. In that case, the compatibility problem almost always disappears. So I believe, like my co-panelist here, that there is some effect but it may not be as significant as we are led to believe.

IGNASIAK (ARC): I think it is worthwhile only to process coal and bitumen together when there are some benefits. If there are no benefits in this sort of processing, I think this exercise is futile. Secondly, I don't really think the problem of compatibility is as simple as that. I think it is actually much more complex. Let me elaborate a little bit on the subject. For instance, if I have a very good hydrogen donor solvent and I am supposed to work with a low-rank coal characterized by 20-25% oxygen content, I don't think we will have something beneficial for the process. On the other hand, if I have a solvent which is low in hydrogen donating capacity, and if I have a caking coal, which by its nature has got a very high caking capacity, this is a good test for coprocessing. So it seems to me that really the compatibility which begins with the coal and solvent is something that we have to work on. As a matter of fact, if we don't have this compatibility right from the beginning, we can, by proper adjustment of the process get this compatibility. Our challenge for marrying the bitumen and low-rank coal was to get this compatibility and what we accomplished is that we use carbon monoxide and steam in order to get rid of the excessive oxygen in the first stage. We simply converted our low-rank coal into high-rank coal in the first stage and then we didn't have a problem. And this is also in response to Dr. Kelly's question regarding the problem of synergistic effects. A synergistic effect, will occur or not occur depending on the chemistry and the chemistry is something that we can really change depending on the steps of the process. You cannot change much chemistry if you apply a one-stage process and hydrogen, and I think we have shown that quite clearly. You've got hydrogen and you've got low-rank coal and essentially there was no synergistic effect but, if you first use carbon monoxide/steam to remove the oxygen then the reactivity of the remaining residual coal is entirely different.

YAN (MOBIL): I would like to respond a little but because this is my belief you don't have to agree to it. When you were thinking of coprocessing to get a synergistic effect, that is, a mutual benefit from it, it takes two sides to tango.

The basic compatibility problem arises because of differences in the reactivity. That is, coal has to be ready to accept some hydrogen and the solvent (petroleum residue in this case) has to be willing to give some. Now you look at the basic reactivity of these two things and they are not the same. That is why you have to adjust the process for it. What are the basic differences? The coals typically are willing to accept, at about 750°F, the donatable hydrogen from the solvent. However, if you look at the petroleum resids, except for a very few, they are not willing to give up hydrogen until 800-825°F. That is where the problem is. Now, how to solve this. You can raise the temperature to keep the thing going. However, this may be too severe for the coal. In that case, what you can do is to have higher temperature but to cut the reaction time very short. That is one way of matching, for example, besides Dr. Ignasiak's approach, which is another one. It's a very good one, I agree completely, but I'm just saying it's a basic principle that I believe in. It is not at all in contradiction to what Dr. Miller has talked about.

PAPIC (BC HYDRO): I have a question for Dr. Ignasiak. In describing your two-stage process for coprocessing, I noticed you used a one-hour residence time. Is that the time you would recommend for commercial processing?

IGNASIAK (ARC): No, absolutely not. The reason that the time was one hour is that we wanted to give the same chance to hydrogen as we were giving to carbon monoxide/steam. I mentioned at one point that carbon monoxide/steam is a very fast reaction. As a matter of fact, it is completed rapidly in about twenty to thirty minutes.

PAPIC (BC HYDRO): What residence time would you recommend for your process in developing it to commercial scale?

IGNASIAK (ARC): As I mentioned, we feel comfortable with about twenty to thirty minutes for the first stage with carbon monoxide/steam.

KUEHLER (CHEVRON): In Dr. Yan's work, I got the impression there was no hydrogen involved at all, yet you ran at 400 psi. Is that right?

YAN (MOBIL): That's correct. Being a sister company, I can tell you this is a visbreaking operation so we try to use conditions very similar to visbreaking. The reason for 400 psi is because you need some pressure to drive through your reaction trains without any recompression and also, I didn't mention this, but most of the time you require some steam to keep from coking and to adjust the flow viscosity through the heaters for heat transport considerations.

KUEHLER (CHEVRON): So, did you introduce steam then, or nitrogen, or an inert gas, or did you control the pressure through the autogenic gases formed?

YAN (MOBIL): In many of the runs you just use the pressure generated because we found that we only ran about one day for each run and I didn't have a problem in making coke to plug up the reactor. So I chose not to add steam into the system to complicate my already complicated system.

VANCEA (OERD/EMR): I have a general question for the panel. It seems to me that in coprocessing coal and bitumen, there are two issues. One is heavy metal reduction and the other liquid yield. Could the panel address the relative merits of the two issues?

KELLY (CANMET): I think from CANMET's point of view we think that overall liquid yield, and in particular distillate yield, is most important as with any single-stage process. I think looking at the results we've seen today, in the CANMET case we're able to generate liquid yields that seem to be as high as those that the Alberta Research Council are talking about in a two-stage process, but we are only using a single stage. The quality of the product looks pretty close in terms of oxygen, sulphur content, nitrogen content and so on. One has to look economically at the two approaches. We are doing work on two-stage processing also to see whether the extra capital cost and process complexity in the two-stage version really is worth whatever gains there might be. I guess from our point of view the decision is not yet clear.

GATSIS (UOP): It all depends on what the end use of the oil is. If you're going to put the oil in any catalytic processes, heavy metals definitely have a big effect. You all know in most cases, particularly in fixed-bed supported catalysts, the metals end up on the catalyst support and they deactivate the catalysts. Boscan crude oil is a very easy oil to convert. The problem is that you can run for maybe a couple of weeks and then you have to throw out the catalysts. So it all depends on what the end use is for the oil that you want to generate.

YAN (MOBIL): Because I work for an oil company, I believe that demetallization, in my opinion, is more important because our refinery operations are unlike those in Canada. Wherever we have a refinery we don't have any coal and vice versa. So to match coal with a refinery operation is strategically quite difficult for us.

STOCKER (UNIV. OF CALGARY): Dr. Kelly, I would like to know the temperature and residence time of your hydrocracking unit?

KELLY (CANMET): As you noticed in my presentation I didn't talk about temperature, pressure and residence time directly. Rather I talked about an overall pitch conversion which is related to those parameters to indicate the severity of operation. It's current policy at CANMET not to divulge the operating conditions at this time.

SHANNON (R.H. SHANNON AND ASSOCIATES): I had the opportunity, Mr. Gatsis, of visiting your labs recently and found one of your old patents using Cold Lake crude. I would like to confirm that we piloted Cold Lake crude this summer with a variety of coals with excellent results and your patent was quite informative. We also found that the demetallization was almost complete in all the product streams using Cold Lake crude. But my questions are to Dr. Kelly: Number one, you said that the CANMET development is proprietary. Why is it proprietary when it is funded totally with public funds? Number two, coprocessing is not in the shared-cost industry programs while all other synthetic fuels and alternate energy forms receive public support. Why is this? Number three, will the Partec Lavalin technical economic study, which you said you had contracted for, also be held proprietary or will it be available to industry and people working in this field?

KELLY (CANMET): Well, let's take the first question. The information is proprietary because CANMET has licensed the hydrocracking process to Petro-Canada, and therefore we are not in a position to talk about operating conditions, just like Mobil or UOP will not necessarily divulge their conditions. Your second question relating to the program funding of coprocessing is somewhat of a political question, and being a technical person I think I'll not try to answer it. Thirdly, the economic study will be proprietary because really coprocessing is an extension of the CANMET hydrocracking process to a greater or lesser extent with a different sort of yield structure and slightly different operating conditions. However, we probably will make a non-proprietary version of that study available for public distribution.

PRUDEN (PETRO-CANADA): Dr. Curtis, in your work with the autoclave, I noticed that you had a maximum in the conversion versus temperature or severity. I've done a little work with autoclaves and we've also seen this kind of maximum. I would like to know what your group thinks the reason for it is?

CURTIS (AUBURN UNIV.): One particular reactor system was a tubing bomb reactor and we differentiate between that and autoclaves. Our reaction system has very quick heat-up between 1 and 2 minutes and very quick cool down in a matter of about 30 seconds. We typically run temperature versus conversion on different types of systems and we do not always see the same results. In this particular system, we did see a maximum of oil conversion at about 425°C and with other systems we see other temperatures. The particular reason for it, I believe, is dependent upon both the coal and the solvent that are present and the chemical interactions that are occurring.

PRUDEN (PETRO-CANADA): Is it possible that it could be hydrogen starvation?

CURTIS (AUBURN UNIV.): In answer to that, I would say we don't believe so. We've done a number of experiments testing the possibilities of hydrogen starvation in which we would add additional hydrogen and react further, or change the size of the reactor and simply have more hydrogen present, and we have found that the conversion results and the product distributions do not change. The second thing that we do is we check for hydrogen consumption and our consumption was at the level of about 20%. So I don't believe that it was hydrogen starvation in this case.

FOUDA (CANMET): Dr. Curtis, you identified your oil products through solubility. Would you be so kind to tell us what was the boiling range of this oil product? And another question, I didn't understand exactly how you distinguished between the coal-originated oils and solvent-originated oils?

CURTIS (AUBURN UNIV.): First question: We have not measured the boiling range of the oil products. Second question: The difference between the two is that we performed thermal and catalytic reactions with the crude residuum material and we then subtracted the amount of oil that was produced for those reactions from the total amount. That was the basic assumption: that we would make the same in coprocessing or that there was not synergy and so then we determined the amount of oil produced. But we did have to make that particular assumption.

RAHIMI (CANMET): Dr. Ignasiak, regarding the hydrogen donorability of bitumen/heavy oils you distinctly mentioned in the title of your paper that bitumens or heavy oils are not hydrogen donors. Do you have any results to support these claims?

IGNASIAK (ARC): Yes, I think it is not only we who actually were working on the subject. As I mentioned, in the introduction to the paper for instance, Dr. Curtis also worked with Lloydminster atmospheric bottoms and you could notice that the conversion values that she obtained for Lloydminster heavy oil were of the order of 20-30%. This is roughly the same result that we got when we used nitrogen instead of hydrogen and carbon monoxide and steam for processing.

RAHIMI (CANMET): Are these results really a direct indication of non-hydrogen donorability? The work at ARC by Dr. Moschopedis clearly indicated that under nitrogen pressure, you have the same amount of conversion in tetralin compared with bitumen or bitumen fractions. So maybe, that is a more direct indication that there is some hydrogen donorability.

IGNASIAK (ARC): I think we are talking about different things. The problem of liquid yields is one problem and the problem of coal conversion is another problem. In any case, if you really wanted to look at or estimate or evaluate the hydrogen donating capacity of the solvent, you have to look at the degree of conversion of your coal, and what I was really trying to indicate is that this degree of conversion was still quite low. We actually have done quite a lot of work in extension of Dr. Moschopedis' work and really the conversions were of the order of 20-30%.

RAHIMI (CANMET): We have direct evidence for hydrogen donorability of bitumen. Later on, if you are interested, we could discuss it.

IGNASIAK (ARC): I certainly would be interested.

RAHIMI (CANMET): Dr. Miller, I didn't see any results given using piperidinopyridine. Could you indicate if there is any increase in coal conversion when you used piperidinopyridine?

MILLER (UNIV. OF WYOMING): Yes there was. I didn't present any specific results from the individual experimental design runs, but at the base case reaction conditions that we chose, the mild condition runs involving either F17, being a poor hydrogen donor, or tetralin, being a good hydrogen donor, with 25% added piperidinopyridine gave coal conversions as high as 87%. That's in 15 minutes, so for coal conversion there was a definite enhancement when that material was present.

RAHIMI (CANMET): Dr. Curtis, have you done any short contact time studies in hydrogen and nitrogen in comparing the results of coal conversion? If I remember your coal conversions, they are all at high residence times.

CURTIS (AUBURN UNIV.): Our experiments are performed at thirty minutes residence time.

RAHIMI (CANMET): And you show that your results in nitrogen and hydrogen are different and your coal conversions are increasing in a hydrogen atmosphere?

CURTIS (AUBURN UNIV.): That is correct.

RAHIMI (CANMET): Have you done any experiments at lower residence times, say 5 minutes or less?

CURTIS (AUBURN UNIV.): No, we haven't.

TAHERZADEH (PETRO-CANADA): Dr. Kelly, have you done any PONA analyses on the distillates that you have in order to identify what type of basic components are included?

KELLY (CANMET): I'll give you a typical distillate analysis, paraffins about 30%, olefins about 2 to 3%, naphthenes about 28% and aromatics about 40%. Of course this will vary given changes in operating conditions.

TAHERZADEH (PETRO-CANADA): What were the yields of naphtha, light gas oils and heavy gas oils?

KELLY (CANMET): That was in the slide I presented on distillate yields for a typical operating case. I can show you the slide later if you wish to look at it.

TAHERZADEH (PETRO-CANADA): Dr. Ignasiak, I was surprised to see the quality of the material you talked about. In fact you mentioned high quality distillate production. Do you consider 3000 ppm of nitrogen in naphtha and also 1.8% oxygen as a high quality naphtha?

IGNASIAK (ARC): No, as a matter of fact, when I mentioned high quality I compared naphtha and medium oil obtained from direct coal liquefaction where we worked roughly with the same coal. In direct coal liquefaction the oxygen content is between 4-5% in naphtha. By comparison we still feel that this is much better and the same occurs with nitrogen.

TAHERZADEH (PETRO-CANADA): Do you have any explanation why oxygen content in the naphtha is higher than in the light gas oil and heavy gas oil although you have worked in a batchwise reactor?

IGNASIAK (ARC): That's a good question. I thought about that, but I can't really come up with a reasonable answer. On the other hand I would like to tell you that if you do direct hydrogenation of coal only, without any bitumen, you will observe the same. The oxygen content in naphtha for some reason is higher than the oxygen content in middle oil.

CLARK (ARC): I would like to address a comment to Dr. Curtis on her results of experiments using hexadecane as liquefaction solvent where she got very high oil yield. And the explanation that I can come up with for this is, that as you solubilize the coal and produce these radical intermediates, which in a normal aromatic coal-derived solvent would in fact undergo radical substitution reactions, and therefore, polymerize to heavy products, in the case of using the purely aliphatic hexadecane such reactions are not possible. Therefore, they're much more likely to react with molecular hydrogen and hence become satisfied as far as their reactivity is concerned and thus converted to lower molecular weight fragments. And I also feel that such an explanation would hold in general for explaining much of the benefits of coprocessing with largely aliphatic solvents.

CURTIS (AUBURN UNIV.): I would like to thank you for your comment.

CLARK (ARC): Dr. Kelly, the aromaticity of your products was very close to that of the original bitumen solvent, I believe about 0.30. Looking at the very good conversion of the coal in these experiments and knowing that the coal is mostly aromatic in nature, I would have anticipated the aromaticity to have increased considerably. I wonder if you could offer any thoughts on that subject.

KELLY (CANMET): We've tried a number of times to get a real quantitative feel for the amount of coal that we are converting into distillate product and I guess at this time we feel that the answer is somewhere from 25 wt % of the coal conversion up to 50 wt % depending upon the operating conditions. I don't believe that a lot of the aromaticity that you see in coal liquefaction products is due to the coal. A lot of sophisticated NMR work has been done to look at coal and I don't think the coal itself is all that aromatic, especially lower rank coal. I think what results in the aromaticity in coal liquefaction is the type of process that has been used to convert the coal because you're always on a fine line between significant coke formation or retrograde reactions and high distillate yields. That is, if you want high distillate yields, you have to be on the fine line, at least with single-stage processes.

BELINKO (PETRO-CANADA): I would like to ask a question of a general nature to the panel members. My question relates to comparisons of different solvents or solvent powers in liquefying coal and a lot has been said about that this morning, especially in terms of batch autoclave experiments. What effort is being made to get a more precise definition of coal liquefaction when there is very little known about the type of residues that are left behind, especially when there are incompatibility problems that may exist in the oil and the coal liquids and the coal residues that could end up as a total residue in the process?

KELLY (CANMET): CANMET recognized that there was a problem in measuring coal conversions in coprocessing some four years ago, because you do generate an IOM and, in general, this IOM does contain certain material that's derived from coal and in the case of using very heavy solvents like bitumens and heavy oils, there is some material derived from that source too. We've spent a lot of time trying to develop a quantitative technique that would allow us to look at the residues and be able to say quantitatively that 30% of this particular IOM material is coal derived and the other 70% is derived from the solvent and so on. It has never been a problem necessarily in coal liquefaction because the solvents are usually tailored to do a good job in liquefaction and therefore they don't coke very much. I guess after looking at a number of sophisticated techniques including FTIR and others, the approach for us that seems to hold some promise is petrography but petrography that is supplemented by other forms of surface analyses or surface observations of these particular materials. I'd like to make a comment to the fundamental research community both here and in the U.S. that I think this is a good research project. What we need is a simple analytical approach that would allow us to take some residue from coprocessing, put it into a machine that is going to do an analysis and generate a weight per cent of IOM from coal and a weight per cent that comes from the solvent. That would allow us to really report true coal conversions and get a handle on other things too.

YAN (MOBIL): It's an interesting and difficult problem but years back we did make some effort in trying to assess that. Because the typical petroleum residues were so messy and converted so easily during coprocessing conditions, we chose a very aromatic narrow cut of cracker bottoms that was so well defined that it generally did not convert at process conditions. So you do the liquefaction and after that you extract it. The aromatics are soluble in very light paraffinic oil-like naphthas, and you can almost quantitatively recover the solvent you started with. The leftover, since it all comes from coal, you may find is mostly asphaltenes at the conditions you are testing. And then we checked the conversion through this method with the calculation based on an IOM basis. They were not too far off, so we thought at least under the mild conditions we were talking about probably the coal was only contributing toward the asphaltenic fraction of the liquid. Now if you have hydrogen and a hydrogenation catalyst in there you are obviously better off.

BELINKO (PETRO-CANADA): Perhaps it might be a better approach to define conversion, especially for coprocessing, not so much in terms of coal conversion but in terms of +975°F (524°C) material and in so doing you know what concentration of that fraction is in the original material, and you can estimate what the conversion of that material is.

KELLY (CANMET): Essentially, some of the data that we showed for CANMET hydrocracking had pitch conversions present and that's what that is and that's why its there. In the feed, all solid organic coal is pitch and then you just look at what the pitch conversion is overall. But it's still challenging. If you want to unravel the complex chemistry of the system you want to know, in the residue, how much is coal derived and how much might be solvent or oil derived, and maybe even more importantly and a much harder problem to solve is how much of your liquid yield is coming from the coal and how much from the solvent. That is really a difficult problem.

Getting back to the coal conversion question. If you assume as most of us here have done, that all the residue is derived from coal or is unreacted coal, then obviously your coal conversion values are going to be conservative. So we're not erring on the wrong side, we're erring on the right side but it still would be nice to have the true answers.

BELINKO (PETRO-CANADA): Dr. Ignasiak, you showed a viewgraph that compared bitumen and bitumen plus coal and you showed the naphtha and gas oil yield from these two cases using two-stage processing. It seemed to me that in the bitumen plus coal case the temperature for a two-stage reaction was higher by about 7 degrees. Could that account for the increase in the gas oil and naphtha yield?

IGNASIAK (ARC): Yes, that's right. Actually those results that you saw were mean values and that's the main reason why there was a divergency in temperatures as far as the second stage is concerned. Yes, undoubtedly, that could result in some additional conversion. Since you noted this problem I would also like to mention at this point that, coming back to your first question concerning coal conversion values or rather not so much coal conversion values as insoluble organic matter, we somehow don't feel that this is something that we should pay too much attention to. Because this amount that we are getting in our process in the form of IOM is really of the order of 1.5 to 2.5%. What we are concentrating on is something which was described on the slide as PE which is a pyridine extract. And it appears that there is great potential with the proper approach for converting this pyridine extract into oils. This is really the major thrust for us now, to convert this 15 to 20% of PE into distillable oils.

SHANNON (R.H. SHANNON AND ASSOCIATES): Actually this question is probably for the Scotia Coal project as much as anyone else. The problem of solid separation has been an unsolved tag-end to coal liquefaction. An appropriate coal solid separation system that displaces the high-cost gasifiers and oxygen plants which can cost as much as the primary unit, would be a great contribution to the industry. They didn't work in Germany and the two-stage operation in Cresap, West Virginia was a mechanical disaster from that end, not from the liquefaction section. I would like the comments of the panel. Do they see the solution of solid separation less of a problem in coprocessing than in coal liquefaction?

YAN (MOBIL): Exactly, it is much simpler than you think. I was very surprised too. Your question of comparison in separating the solid from the product is much easier in the coprocessing case compared with coal liquefaction using anthracene oil. We have worked on this extensively and I hope one of these days we will be able to discuss it.

SHANNON (R.H. SHANNON AND ASSOCIATES): The part that worried me was although there is less ash in the system, perhaps certainly less than half, I wondered if the ash and unreacted coal and resid ratios at some stage in the system ended up the same as they did in coal liquefaction and therefore there still was the same kind of problem, or if there was a different ratio?

YAN (MOBIL): It could be, but I doubt it.

KELLY (CANMET): I would think that the same problem exists. If you get a very high ash coal and you want to have a very high liquid yield, then by necessity you are going to have a very small amount of residue when you have that very high yield, and all the ash is going to be in the residue, just like in coal liquefaction. You can easily get into a situation where you will have a residue with a 50% or greater ash content and then you have potentially, if you want to use that residue, a solid separation problem, that distillation, for example, won't handle. With the results we showed today in CANMET coprocessing with the highest coal concentrations we experimented with, I think, if I remember correctly, and I think Dr. Fouda could verify this, I think the ash content in our residue was less than 36 to 37 wt %. So theoretically, I suppose vacuum distillation could still be applied. However, we're also looking at other techniques like spherical agglomeration to take mineral matter out at the front-end and, of course, the Sandwell-Beak process to allow us to do a clean separation downstream. So, I don't necessarily agree with Dr. Yan. I think in this respect coprocessing has the same problems as coal liquefaction. What might make a difference is if the solid/liquid characteristics are different enough in coprocessing so that the various physical phenomena that are used for the separation might work better than they do in coal liquefaction. For example, anti-solvent de-ashing might work better because the chemical and physical characteristics of the solid and the liquid in coprocessing make that the case compared with coal liquefaction.

IGNASIAK (ARC): I would have a little bit different opinion on the subject. First of all, really we are interested in coprocessing as a process which eliminates the recycling mode of operation. If we dispose of the recycling mode, and if we put something in front of the process, and if we can bring down the ash content in our typical Alberta coal from let's say 27% to 5% and it appears that this is possible, then obviously after diluting with bitumen we have only about 1.5% and that, I think after disposing of the recycle mode, really has considerable advantages.

MIKHLIN (SNC): I would support what was said by Dr. Kelly. In principle, in beginning with a source of coal with a high-ash content and if it could not be taken out before the process, then definitely you will experience the same problems as in direct coal liquefaction, unless you would like to discard some of the residue and some of the energy contained in this residue. So it is really a case of economics. If you would like to utilize all the energy in the coal and in the residue then definitely the same problem will exist in both cases.

FOUDA (CANMET): I have a minor correction to make to Dr. Kelly's earlier comment on the ash concentration that we have experienced. Our residues would contain 36% insoluble matter, including ash and inorganic insolubles, but not only ash.

KELLY (CANMET): I would like to ask Mr. Gatsis a question. A lot of results were presented today, but the impression I got as I was sitting back trying to look at this was that if I had to grade the processes that we heard about in terms of distillate yield, we'd probably have something like Alberta Research Council at about 70 wt %, and I haven't verified the figure but that's what Dr. Ignasiak mentioned. CANMET has distillate yields at about 75% or so and, it looked like Mr. Gatsis with UOP's process was really up there with 85% or at least 80% anyway. The total oil was around 90% in one case, for the catalytic mode. The question I would like to pose Mr. Gatsis is that in CANMET hydrocracking, our biggest operational problem is always related to coke formation and if we want more distillate yield we are always running into potential coke production. Could you comment on how UOP gets up to 90 wt % oil yields and still doesn't have any operational problems?

GATSIS (UOP): The main reason that we can have a high liquid yield is we try to maximize liquid yield. There are many refining operations in a refining flow scheme that are suited for taking a good quality oil and doing whatever you want with it. And if you look at some of the costs of doing things, the big cost is going from a very heavy material into something that a refinery can use. Once a refinery can use a feedstock, they're home free, so to speak. So what we try to do is, we don't try to do everything in the first stage, in the first part of processing. Our main objective is to come out with the high quality syncrude. You may have noticed that the products that I showed you had very low metal content; they had very low asphaltene content; they also had some distillate and some gas oil material but they had an appreciable amount of heavy ends. These heavy ends are something that a refinery can use, they go into a hydrotreater so you can convert them into whatever else you want.

BELINKO (PETRO-CANADA): I would like to follow up on this point. In catalytic liquefaction work, especially work that involves batch autoclaves and small units, do you generally use fresh catalysts? If so, how do you compensate for the initial activity of the catalysts which tends to give sometimes very high and very misleading conversions and yields and so on? I heard Dr. Curtis this morning talk about the use of catalysts and again Dr. Kelly's comment about the UOP data.

KELLY (CANMET): I think that's a real problem and I've seen a lot of papers dealing with very sophisticated mathematical models that try to simulate the aging effect that occurs. We don't work in a direct supported heterogeneous catalytic type of mode at CANMET. We have chosen the disposable mode and so we haven't bothered to pursue studies that would try or attempt to do this simulated aging, at least for the primary processing step.

CURTIS (AUBURN UNIV.): Could you restate the question please?

BELINKO (PETRO-CANADA): Generally, when you start with a fresh catalyst you tend to presulphide it first and then you condition it, precoke it in some way, so that you remove the initial high activity of that catalyst. If you don't do this precoking step and you start working with the catalyst right away, there's an initial high activity associated with that catalyst which can give rise, especially in batch autoclave tests where you tend to use fresh catalysts all the time, to very high misleading conversion values until that initial activity would be lost. This would not occur in commercial practice because that initial activity would be lost in days, perhaps, and then you would reach some steady state of activity level that would be much lower than that initial activity.

CURTIS (AUBURN UNIV.): So what you're really asking is related to the controversy that rages between using an initial catalyst activity versus an aging effect. There are two definite opinions on that particular subject. We use the catalyst as it comes out from the presulphiding step and we have not tried to age it in any manner. We are working in the initial high activity region. We have another contract with the Department of Energy where we are trying to use our knowledge of catalyst activity and catalyst development to develop catalysts that have longer term activity and so what we would like to see is a catalyst that would maintain that high initial activity.

GATSIS (UOP): The autoclaves that I used were for a preliminary stage of work in the first phase of the operation in trying to develop the process. In the autoclave you're definitely not going to get stability or deactivation data generated from the run. But you follow up the autoclave run with continuous plant runs to get the data you need.

KELLY (CANMET): It could explain why the liquid yields might be higher when you're comparing our results which are continuous bench-scale results using a non-supported catalyst versus autoclave results with a supported catalyst with a very high catalyst activity.

GATSIS (UOP): In answer to that question, we have been able to correlate our autoclave activities with continuous operation. So the results I presented, although they may be batch results, we think are very valid results.

KELLY (CANMET): I think that HRI gets around the problem by replenishing the catalyst at a given rate, and that's one way of doing it, to make up for the loss of activity. Other people temperature-program the reactor slightly as the catalyst starts to deactivate, to keep the reactivity level roughly constant, until the temperature gets so high they run into a severe coking problem, and then they have to regenerate.

MIKHLIN (SNC): I have a question along the same line, concerning the UOP process. I understood that you are using high activity catalysts. One of the results of the first stage, one-stage process is substantial reduction in the metal content. A high amount of metal would definitely result in rapid deactivation of the catalyst which means that unless you have a special catalyst, which has very good resistance in this case, the catalyst consumption would be quite high. If the catalyst is active it would likely be a very expensive catalyst. So the same problem as in the H-Coal process will be encountered, if you are using a high activity catalyst directly in contact with a slurry having high metal content.

GATSIS (UOP): I'm not at liberty to give you an answer on that question.

IKURA (CANMET): Dr. Ignasiak, I seem to recall that you mentioned a hydrogen consumption of approximately 1% or less for the CO/steam case. Should I take that as a hydrogen equivalent consumption?

IGNASIAK (ARC): What I meant by saying that there is about 1% consumption, is that under normal conditions when you hydrogenate the coal with hydrogen you need about 6-7% by weight of hydrogen from external sources. In this case because you do generate a considerable amount of hydrogen in your first reactor and because your deoxygenation takes place only exclusively with carbon monoxide, the need for hydrogen from an outside source is reduced to about 1%, on a slurry basis.

IKURA (CANMET): I have been interested in this mechanism of first-stage reaction and was wondering if you looked into the differences of qualities of the reactants coming out of the first-stage reactor when you use CO/steam and hydrogen only?

IGNASIAK (ARC): The first stage is the stage which converts coal with high efficiency into soluble product and reduces the oxygen content from about 20% to roughly 5%. We are not really very much concerned with what else happens in the first stage. We are obviously not producing during the first stage considerable quantities of distillable products. It is sort of a pretreatment, a deoxygenative pretreatment, that really, in addition to what I said there are some other things going on already in the first stage which have a very beneficial effect on hydrogenation in the second stage.

IKURA (CANMET): I think that there is a distinctive difference in the reaction mechanism when you use CO/hydrogen in terms of making a liquid product.

IGNASIAK (ARC): There is no doubt about that. Really it's mainly a deoxygenation and solubilization reaction with very little cleavage taking place.

STOCKER (UNIV. OF CALGARY): Dr. Yan, I'm very intrigued by the fact that you didn't get any coke deposition when you used 100% residue. Even when you do visbreaking of propane you do get coke deposition. Was there a lining on the walls of the reactor?

YAN (MOBIL): Because of the very short residence time, no more than five minutes, and you have to run that away, I would say, no, generally defining coke with a cut-off point of 0.5% toluene insoluble. You are not going to make more than that. At these conditions some of the residues may coke very quickly, some others won't and for this particular residue we wanted to make sure at that condition that we didn't make too much coke to confuse the picture. That's why we do preliminary results first.

CLOSING REMARKS

KELLY (CANMET): I think we have had a good meeting, a good three-day meeting. What impressed me is the degree of interaction we are developing in Canada between the different groups. It's really encouraging to see the Nova Scotia Research Foundation cooperating with the University of Regina to do petrography on their samples. It's also encouraging to see the different groups in B.C. getting together where there is common ground and I think that if we keep going, this situation cannot but improve, and of course, that's just what we are looking for nationally.

Personally, I feel that the quality of papers at this meeting improved over the papers at our first meeting. I'm not saying that the papers at the first meeting were not good, I just think that those at this meeting were that much better. I think it's going to be a challenge for us to have even a better third Coal Conversion Contractors' Review Meeting, hopefully in two years. I am also impressed with the large foreign attendance that we have had, particularly from the U.S., at this particular meeting. I guess the coprocessing session was really the significant factor in causing this but I hope it will continue, and I hope that there will be much better cooperation between Canada and the U.S. in the area of coprocessing and other synfuel areas.

Looking back at the sessions that we have had, I think in international cooperation we have only scratched the surface. We have a program with Japan and the door is open for more interaction with West Germany. I think the challenge is there both to provincial R&D organizations as well as to industry to walk into the open door and see if we can have more development. The cost of R&D in synfuels is such that I think we just have to look at international cooperation to some extent. And, of course, in the Canadian sense or situation it's more important because we don't necessarily have the large industrial manufacturing base that we really need to bring synfuels right through to commercialization. So we are going to need some outside help, I think, and these programs are a way to get communication started so that can happen.

In pyrolysis/fundamentals we have seen how different technologies like petrography can aid our understanding of what's happening in a complex chemical reacting system. We have seen novel approaches like the liquid clathrate system that have potential to reduce overall operating and capital costs. It doesn't bother me, that after two years into that project, we haven't seen a commercial process developed. I'll be happy after three years if we have just scratched the surface. The main point is that it's not everywhere that you'll see researchers taking on this sort of challenge. Everybody likes the cleaner system, the more well-known system, but when you branch off into a new area of chemistry like this, you really are breaking the frontiers. And you know that at CANMET we're open to unsolicited proposals and we are ready to listen to novel concepts in this sort of vein.

In gasification, we've seen that the indirect route can be economic. I mean a DCF of 17½% is pretty good, even with government subsidy. I get a little discouraged at times because when you talk about the economics of direct coal liquefaction, any sort of direct coal liquefaction, it's always the same result. A barrel of syncrude from direct hydroliquefaction is double the current natural crude price. So here we have a situation, using indirect liquefaction, that looked pretty close to being economic and maybe we should look harder at these other alternatives.

In coprocessing, well, what can I say. I think we had a terrific session. It's not every day that we bring together a group that has the kind of expertise that we have had here today, both in the audience and in the panel. I just hope that we will continue to do this sort of thing, officially or unofficially, in the future.

Finally, and not the least of matters to talk about, I would personally like to give special thanks to all the session chairmen: Mike Papic, Jean Denis, Duke duPlessis, Don Abbott, and of course, Basil Parsons substituting for David Brown. Special thanks have to go to Joan Beshai of our Technology Information Division, CANMET, who really handled all of the administrative details. Even though Jean says I was instrumental, I basically looked after the technical aspects, and it was really Joan who interfaced to make sure everything went right administratively. The group from the Association Management Centre, Majorie Zingle, and Valerie and the others did a splendid job of keeping everything on track. Special thanks to Nita Harcourt for handling the report display and preparing the list of final reports for distribution.

Lastly, I would like to thank our Director, Dr. Basil Parsons, of the Energy Research Laboratories, for his kind and significant encouragement and support, not only to me, but to everybody involved at CANMET in making this meeting a success. Overall, I think it was a great meeting; I thank you very much, and I hope that all of you have a good trip home.

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Coal conversion in Alberta: Stage 1	Algas Resources Ltd.	18SQ.23440-6-9086-1	OSQ76-00158	M. Ternan	Sept. 1977	82-4611 82-4612	582
Coal liquefaction plant feasibility study	Algas Resources Ltd.	18SQ.23440-8-1925-4	OSQ79-00130	M. Ternan	March 1981		
Phase I – Executive summary						82-2973	17
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Petroleum coke – supply, demand, cost 1974-1990 and technical and economic appraisal of pure electrode coke by solvent refining of Canadian coals	Aluminum Company of Canada	18SQ.23440-6-9086-9	OSQ76-00156	D. Montgomery	April 1978	(Backfile)	67
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Liquefaction of low rank coals – Phase I	Beak Consultants	18SQ.23440-7-9059	OSQ77-00131	J.F. Kelly	May 1978	(Backfile)	267
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Investigation to determine the feasibility of using bitumen as solvent for coal liquefaction – Phase I, II	Sandwell Beak Research Group	19SQ.23440-8-9104-1 19SQ.23440-0-9047	OSQ79-00100 OSQ80-00067	J.F. Kelly	Jan. 1980	Confidential	

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Demonstration and testing of the use of H_2S as a promoter in coal liquefaction	Sandwell Beak Research Group	23SQ.23440-3-9198	OSQ83-00185	P.M. Rahimi		Confidential	
A study to evaluate and compare the production costs of liquid fuels from coal and from oil sands in Alberta	Dynawest Projects Ltd.	23SQ-23440-1-9059	OSQ81-00113	H. Sawatzky	Feb. 1983	Available Jan. 1985	125
Production of liquid fuel from coal progress report no. 1	Inco Metals Co.	O1SU.23440-7-9123	OSQ77-00184	J.F. Kelly	March 1978	(Backfile)	42
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Supercritical gas extraction of Canadian coals	Raylo Chemicals	23SQ.23440-8-9091	OSQ79-00114	A. George	Feb. 1982	80-4659	30
Supercritical gas extraction of coal: investigation of the chemical and physical factors	Raylo Chemicals	23SQ.23440-0-9111	OSQ80-00186	P. Sears	April 1982	(Backfile)	81
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Quantitative analysis of coal in the presence of coke using Fourier transform infrared spectroscopy	Raylo Chemicals	26SQ.23440-2-9096	OSQ82-00109	P. Rahimi	April 1983	Confidential	
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The design, construction and commissioning of a bench scale hydrogenation unit	Stearns Catalytic	14SQ.23440-9-9150	OSQ80-00095	M. Ikura	Dec. 1983		17
Characterization of solid residues from coal liquefaction processes, Phase I	University of Regina	14SU.23440-9-9177	OSU80-00088	J.T. Price	March 1981	82-4620	292
Characterization of solid residues from coal liquefaction processes, Phase II	University of Regina	20SU.23440-0-9160	OSU-00105	J.T. Price	March 1982	Confidential	212
Characterization of solid residues from coal liquefaction processes	University of Regina	OIST.24440-0-9102	OST82-00067	J.T. Price	June 1983	84-0756	144
Characterization of solid residues from coal liquefaction processes	University of Regina	24SU.23440-3-9113	OSU83-00127	W.D. Dawson	May 1984	Confidential	
Study relating to the technical and economic feasibility of lignite liquefaction in Saskatchewan	Saskatchewan Oil & Gas Corp.	23SQ.23440-2-9203	OSQ82-00269	L. Mysak	Oct. 1982	84-3984	1251
Determination of rheological properties of coal-oil slurries	Saskatchewan Research Council	18SQ.23440-7-9073-VII	OSQ77-00263	G.N. Banks	Feb. 1981	82-1535/2	102
Technical assessment of coal liquefaction processes for Canada	SNC	18SQ.23440-9-9036	OSQ79-00090	M. Ternan	Sept. 1981	82-3658 82-3666	1387
Beneficiation of coal by oxygen removal	SNC	18SQ.23440-8-9090	OSQ82-00110	E. Furimsky	March 1983	Available Dec. 1984	43
Investigation to develop innovative methods for the removal of oxygen from coals	SNC	23SQ.23440-1-9034	OSQ81-00053	E. Furimsky		Available Dec. 1984	42
Determination of the feasibility of designing process development unit for the commercialization of a spouted bed gasifier	SNC	23SQ.23440-1-9063	OSQ81-00193	G. Sirianni/ M. Skubnik	July 1982	83-2873	174

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Application of fluid bed gasification technology and absorbents (dolomite, limestone, oil shale) for utilization of high sulphur New Brunswick coal	SNC	23SQ.23440-2-9104	OSQ82-00158	D. Fung	Jan. 1983	Available Dec. 1984	113
Technoeconomic evaluation of synthetic fuels from coal-heavy oil mixtures	Synthetic Fuels Associates	O3SQ.23440-2-1940	OSQ82-00133	J.F. Kelly/ M. Ikura	Jan. 1983	Confidential	
Short residence time pyrolysis of coal	University of Waterloo	20SU.23440-1-9032	OSU81-00087	J.F. Kelly/ S. Fouda	June 1982	83-0025	72
Screening program on short residence time pyrolysis of coal	University of Waterloo	14SU.23440-2-9101	OSU82-00255	S.A. Fouda	June 1984	Available 1985	126
Direct coal liquefaction under ambient conditions	University of Victoria	12ST.23440-4-9029	OST84-00012	P.M. Rahimi		Confidential	
Characterization of liquid fuels from spouted bed pyrolysis of Canadian coals	University of British Columbia	20SU.23440-2-9093	1SU82-00245	M. Skubnik	July 1984	Available Dec. 1984	157
Spouted bed gasification of Western Canadian coals – Final report 1979/80	University of British Columbia	18SQ-23440-8-9111	OSU79-00065	G.V. Sirianni	April 1980	80-4670	40
Spouted bed gasification of Western Canadian coals – Final report 1980/81	University of British Columbia	20SU.23440-0-9152	OSU80-00068	G.V. Sirianni	May 1982	83-2866	39
Spouted bed gasification of Western Canadian coals	University of British Columbia	20SU.23440-0-9143	OSU81-00074	G.V. Sirianni	May 1982	83-2866	39
Continued study of spouted bed gasification of Western Canadian coal	University of British Columbia	OSU.23440-2-9000	OSU82-00138	K. Thambimuthu/ G. Sirianni	May 1983		44
A review and assessment of processes for indirect liquefaction of Ontario lignite into methanol and other liquid fuels – A 50/50 shared-cost contract	Ontario Energy Corp.	17SQ.23440-2-9092	OSQ82-00201	D. Fung	June 1984	Confidential	82 + App.
A study of the suitability of British Columbia and Nova Scotia coal resources for underground gasification:	B.H. Levelton & Associates						
Phase 1 – Underground coal gasification technology and site selection criteria		23SQ.23440-9-9175	1SQ80-00057	R. Sage	Jan. 1981	82-1531	143

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A study of the feasibility of underground coal gasification in the Bowron and Tulameen coalfields of British Columbia	B.H. Levelton & Associates	23SQ.23440-2-9018	OSQ80-000217	D. Fung	Feb. 1983	84-043	127
Development of bench scale fluid bed gasifier and gas burner system	Carleton University		OSU77-00413	L. Mysak	Aug. 1979	80-0494	79
Product control in fluid-bed gasification and low BTU gas burner	Carleton University	8-9112	OSU78-00368		May 1980	81-1174	33
Shaunavon coal utilization study:	Saskatchewan Power Corp.						
Phase I – 300 MWe AFBC fired power generation plant		18SQ.23440-8-9059	OSQ78-00110	G. Sirianni	April 1979	Available Dec. 1984	79
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Small gasifier applications	Saskatchewan Power Corp.	18SQ.23440-7-9055-2	OSQ78-00019	G. Sirianni	Feb. 1979	81-1909	172
Gasification and petrographic studies of Saskatchewan lignites	Saskatchewan Power Corp.	18SQ.23440-7-9073	OSQ78-00023	G. Sirianni	April 1979	75-5516	216
A technical and economic assessment of the reactivity of Saskatchewan lignite coals as they relate to gasification processes:	Saskatchewan Power Corp.						
Lignite reactivity – II		18SQ.23440-8-9125-1	OSQ79-00053	L.P. Mysak	May 1980	80-4665	116
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Phase IV – Final report		23SQ.23440-0-9139	OSQ81-00093	L.P. Mysak	April 1983	84-1278	70
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Study of high temperature gas clean-up	Ebastec Lavalin	03SQ.23440-2-9021	OSQ83-00127		May 1983	84-1182	275
Development of fluid bed gasification control parameters for a range of Canadian coals:	Asecor Ltd.						
Phase III – Final report		13ST.23440-9-9149	OST80-00006	L. Mysak	Nov. 1981	83-0054	93
Phase IV – Final report		23SQ.23440-9-9140	OSQ81-00036	L. Mysak	July 1982	83-2111	56